

ANNALS OF THE NEW YORK ACADEMY OF SCIENCES

VOLUME 82, ART. 3 PAGES 645-796

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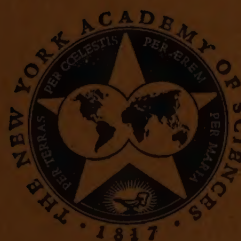
## RADIATION AND HIGH-TEMPERATURE BEHAVIOR OF TEXTILES

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NEW YORK

PUBLISHED BY THE ACADEMY

October 7, 1959

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J. J. PRESS

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\* This series of papers is the result of a conference on *Radiation and High-Temperature Behavior of Textiles* held and supported conjointly by The New York Academy of Sciences, the Polytechnic Institute of Brooklyn, and the United States Navy Clothing and Textile Research Laboratory, Brooklyn, N. Y. on November 14 and 15, 1958.



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## INTRODUCTION

J. J. Press

*Institute of Polymer Research, Polytechnic Institute of Brooklyn, Brooklyn, N. Y. and United States Navy Clothing and Textile Research Laboratory, Brooklyn, N. Y.*

World War II with its V-2 rockets and atomic bombs shattered conventional military concepts and introduced a new age of unbelievable power, speed, and long-range capabilities. These and other accelerated scientific advances already provide mankind with the means for overcoming many worldly ills and limitations; they also provide man with a means for destroying himself. These developments call for a critical reappraisal of man's material needs; this publication represents a combined effort on the part of industry, education, and government to evaluate these needs in the textile field.

An effort is made in this publication to cover representative problems and needs in clothing, parachutes, reinforced plastics (missiles, nose cones), and radiation chemistry; protection against fire and against intense thermal radiation (atomic); and fiber research to reduce melting, burning, and radiation hazards.

This introduction would be incomplete without acknowledging the labors of the contributors to this monograph, the very effective participation of Hoyt C. Hottel of the Massachusetts Institute of Technology, Cambridge, Mass., of John H. Dillon of the Textile Research Institute, Princeton, N. J., as chairmen of the several sessions of the conference, and of Herman F. Mark of The Polytechnic Institute in initiating and holding the conference on which this monograph is based.

## INTRODUCTORY REMARKS WITH SPECIAL REFERENCE TO TRANSPORT MECHANISMS

Hoyt C. Hottel

*Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Mass.*

Research on the effects of high-intensity irradiation of textile materials was initiated about a decade ago, much of it under the auspices of the Armed Forces Special Weapons Project. A number of the research groups involved from the beginning are represented in this publication. I suspect most members of these groups thought ten years ago, as I did, that they were embarking on a modest research program on a problem that would be solved in short order. However, research in this field, as in most others, has a way of spawning new problems faster than it solves old ones. It is fitting and timely that The New York Academy of Sciences, the Polytechnic Institute of Brooklyn, and the United States Navy Clothing and Textile Research Laboratory, Brooklyn, N. Y., have instigated the publication of this monograph to review the progress made and to speculate on new developments.

The problems related to the response of textiles to high-intensity thermal radiation may be divided into 4 categories; (1) those properties of textiles significant to the problem; (2) the mechanism of heat transport through irradiated fabric; (3) the condition for burn-production in clothed skin; and (4) the development of textiles that will give greater protection to the skin and be less affected themselves in the process. I shall discuss briefly three of these categories and elaborate somewhat on the second.

*Properties.* These include the physical properties—thermal conductivity, density, specific heat, and their change with temperature, if large; the spectral reflectance and transmittance; their change with temperature (and it may be large); the conversion of spectral to total values by integration over the spectrum of the sources; and the smoke-forming tendency, unless that has been included as an effect on reflectance and transmittance. However, more sophisticated treatment of some of these properties may be needed if they are to be used for quantitative study of the energy transport mechanism. For example, over-all reflectance and transmittance may not suffice; it may be necessary to allow for multiple scatter to prevent mistaken extrapolations to new systems.

*Burns.* A good summary in this field is contributed to this monograph by George Mixter. It appears that those combinations of time and flux rate at the skin surface that produce burns are now well established and that, in consequence, the function of animal experiment is to study the burn problem and not to assess textiles.

*Developmental activities.* Whether headway will come from new ideas on weave structure, from changing the fiber reflectance, from incorporating encapsulated solids the covers of which melt and react endothermally or produce smoke or intumesce on heating, from use of more resistant fibers capable of holding their built-in protection despite thermal punishment—these are ques-



tions that are also discussed in this publication. In any event, progress in this field is intimately related to an understanding of the heat-transfer process.

### *Mechanism of Heat Transfer*

Guidance on the problem of how the measured properties of a fabric affect its protective value, and on what properties one seeks to build into a new fabric comes from an understanding of the mechanism of heat transport through irradiated cloth. A little consideration indicates how complex this mechanism of heat flux can be. Consider living skin covered with a layer of cloth and subjected suddenly to high-intensity irradiation. In part, this penetrates directly to different depths in the cloth (because of open texture or fiber diathermancy or both) and is absorbed; in part, it is reflected back out from the surface and from the interior by multiple scatter; and in part it passes unobstructed through the cloth pores to the skin surface and is absorbed. The heat arriving at the skin surface by direct transmission is later joined by heat arriving by conduction through the cloth; the latter is affected both by outward convection and back-radiation loss from the cloth and by the thermal resistance presented by an air gap between cloth and skin—a resistance produced by cloth nap and cloth wrinkles as well as by the hairiness of the wearer. Superimposed on these already complex phenomena are others that are much more difficult to analyze—the effects of moisture and of thermal decomposition in the cloth. The cloth moisture tends to move through the cloth, some inward and some outward, as the heat wave moves in. The moisture moving in and recondensing furnishes a rapid means of energy transport toward the skin, and the condensing tars from thermal decomposition of the cloth increase the effect; however, as the inside cloth and skin temperatures continue to rise, this accumulated moisture begins to evaporate and move back out through the cloth, simultaneously absorbing energy of vaporization or desorption at or near the skin and producing a late-stage protection in contrast to the early-stage punishment associated with the moisture in the original cloth. To add one more item, one well-known, to this accumulating complexity, decomposition of the outer layer of the cloth may set in and yield a smoke that absorbs or scatters some of the incoming radiation.

*Skin simulation.* To understand the mechanism of heat flux through irradiated cloth to skin one must have a way of testing any theory developed, as by comparing predicted fluxes or temperature patterns with experimentally determined ones. However, experiments on animals are notoriously time-consuming for many reasons, not the least of which is the variability of the subject. Consequently, a skin simulant is needed. A simulant must present to the overlying cloth no detectable difference, thermally, from live skin, since the response of the cloth will otherwise be atypical. Consider the irradiation, with equal time-intensity patterns, of three samples of the same cloth, covering respectively a thick slab of copper, live skin, and a slab of foam glass. An irradiation impulse on the second specimen that would raise the outer cloth surface temperature to 120° C. and the skin surface to 60° C. and produce a mild skin burn would heat the cloth specimen over the copper to perhaps 50° C.



on its outside face and would hardly raise the temperature of the cloth-copper interface. This same impulse falling on the third specimen could scorch the outer cloth surface and raise the temperature of the foam-glass surface to a value that, on human skin, would produce major destruction. One of the non-simulant materials could not even be relied upon to yield *relative* protective values of two different cloths because their respective heat-transfer mechanisms might be so different—one, for example, by conduction and one by diathermancy—as to cause a reversal of relative values when tested on the wrong kind of heat sink.

A material may be said to simulate skin when, in response to the same surface-flux-versus-time curve (whether by radiation or by any other mechanism of transport to the surface), there is for every depth  $L_s$  below the surface of the skin (including 0) a corresponding depth  $L_{ss}$  in the simulant where the temperature-time pattern is identical. This will be true when two conditions are met: (1) When the steady-state resistances to heat flow from surface to  $L_s$  in the skin and to  $L_{ss}$  in the simulant are equal, that is,

$$L_s/k_s = L_{ss}/k_{ss} \quad (1)$$

where  $k$  is thermal conductivity; and (2) When the heat-storage capacities between the surface and  $L_s$  in the skin and  $L_{ss}$  in the simulant are equal, that is,

$$L_s \rho_s c_s = L_{ss} \rho_{ss} c_{ss} \quad (2)$$

where  $\rho$  and  $c$  are density and specific heat. Eliminating  $L_s$  between these relations yields

$$k_s c_s \rho_s = k_{ss} c_{ss} \rho_{ss} \quad (3)$$

the necessary and sufficient condition for simulation. It is seen that the simulant need not have the same values of  $k$ ,  $c$ , and  $\rho$  as skin; it need only have the same value of their product. With this condition satisfied, but with  $k$ s different, the corresponding points in the skin and simulant will be related by

$$L_{ss}/L_s = k_{ss}/k_s \quad (4)$$

a ratio that may be referred to as the stretch factor  $a$  of the simulant.

The possibilities of various materials as skin simulants may be presented graphically by plotting their properties,  $k$  versus  $c\rho$ , on logarithmic coordinates (FIGURE 1). On such a plot lines of constant  $k c \rho$  are straight, of slope  $-1$ . Included on FIGURE 1 is "standard" human skin according to a definition adopted at an AFSWP conference. Through this point is a line of constant  $k c \rho$  ( $8.5 \times 10^{-4}$  cal.<sup>2</sup>/cm.<sup>4</sup> C<sup>2</sup> sec.), on which all skin simulants must lie; the stretch factor  $a$  ( $\equiv k_{ss}/k_s$ ) is marked along the line. Examination of the thermal property data indicates that polyethylene, once considered for skin simulation, is too far off the line and produces excessive skin-surface temperatures; that silica glasses and asbestos cement of the right composition are quite good simulants, with a stretch-factor of the order of 2; that the metals, unmodified, are of course unacceptable; that no isotropic material has been found with a high stretch factor.

High stretch factors have two particular merits. If the temperature pattern in depth in skin covered by cloth is to be used as a measure of whether a proposed mechanism of heat transfer through the cloth is valid, accurate placement of thermocouples in depth in the simulant is necessary; and the depths most sensitive to error in the assumed mechanism are quite near the skin surface. Placement of a couple reproducibly 0.5 mm. below the surface is quite

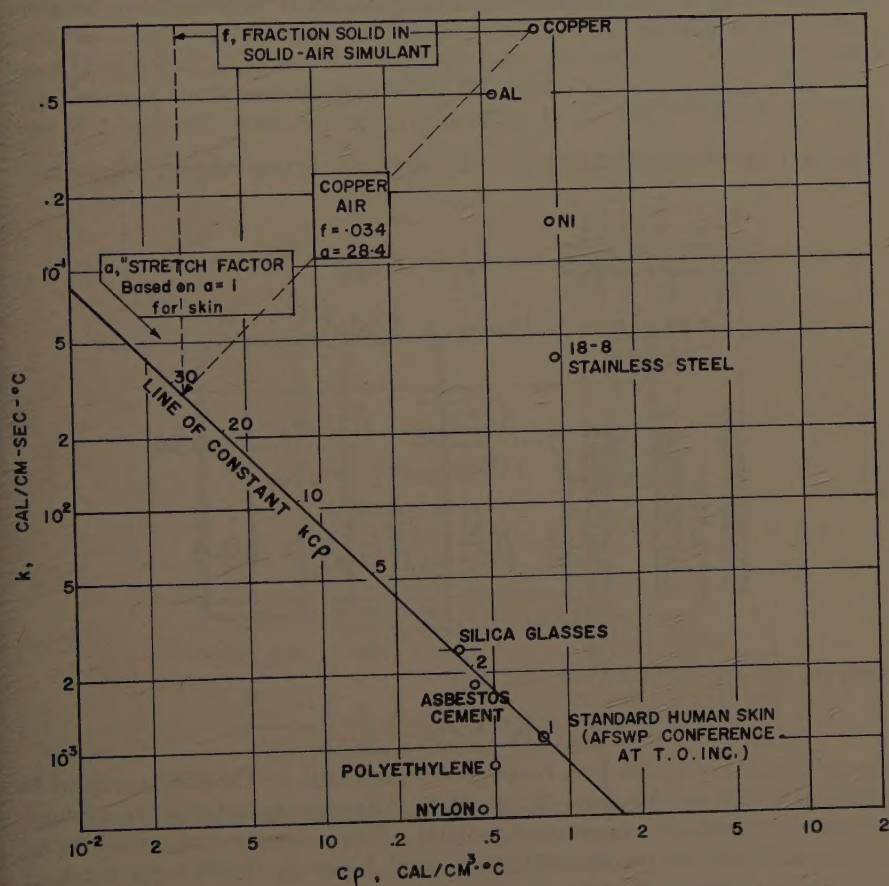


FIGURE 1. Graphic representation of the principles of skin simulation.

difficult, and a stretch factor of 20 would greatly improve the accuracy possible. Moreover, the statement that two different combinations of exposure time and intensity produce the "same" degree of burn cannot be true except for some arbitrary criterion of "sameness," such as appearance. The burns are in fact different in their depth of penetration and, probably, in their healing. Progress in this more complete assessment of burns can be aided by the provision of a technique for establishing the detailed time-temperature-depth relation in skin under clothing; the simulant with a large stretch factor can be helpful here.



Copper has been said to possess too high a conductivity for use as a simulant. However, the desired lower conductivity  $k_{ss}$  can be imitated by arranging copper in parallel air-spaced fins attached to a surface plate (FIGURE 2). Except for the heat-flow resistance in the surface plate (which can be made negligible or partially allowed for), the heat-flow path, compared to that of continuous matter, is reduced to the fraction  $f$ , the volume fraction of the simulant which is copper. The heat-storage capacity is reduced in the same ratio. These relations are

$$k_{ss} = f k_{Cu} \quad (5)$$

$$(c\rho)_{ss} = f (c\rho)_{Cu} \quad (6)$$

The necessarily fixed property of a skin simulant is the value of  $k c \rho$ ; by mul-

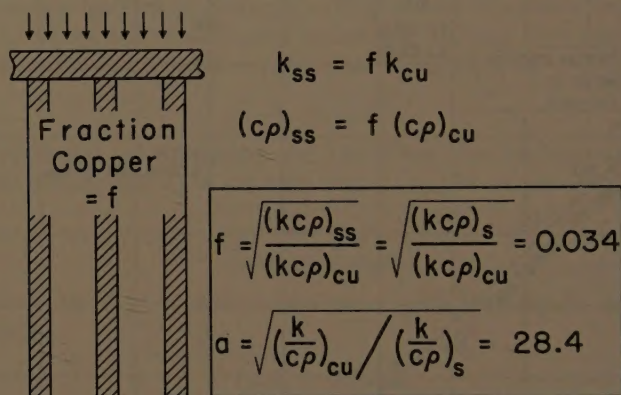


FIGURE 2. Copper simulant.

tiplying EQUATIONS 5 by 6 one sees that

$$f = \sqrt{(k c \rho)_{ss} / (k c \rho)_{Cu}} \quad (7)$$

Since the value of  $k c \rho$  for pure copper is 0.74 and that for the simulant must be identical to that for skin itself ( $8.5 \times 10^{-4}$ ), the necessary value of  $f$  in a finned-copper skin simulant is established as 0.034. The corresponding stretch factor  $a$  is  $k_{ss}/k_s$  which, by use of EQUATIONS 5 and 7, can be shown to be given by

$$a = f \frac{k_{Cu}}{k_s} = \sqrt{(k/c\rho)_{Cu} / (k/c\rho)_s} = 28.4$$

This high stretch factor permits the determination of a temperature 0.5 mm. below the skin surface by soldering a thermocouple 14 mm. down along one of the copper fins of the simulant.

Two practical variations of the copper simulant appear in FIGURE 3. The left sketch, with thickness of fins greatly exaggerated, shows a simulant made by soldering flanged plates to a heat-collecting surface (the "skin" surface), bending their other ends to minimize air circulation, and attaching, at right angles to the plates shown, pairs of end plates to close the air spaces and com-



plete the guard-ring effect around the central portion of the fins, where temperatures are measured. Additional aid to prevention of lateral heat flux is provided by vertical slitting of the fins on either side of the regions occupied by thermocouples. The right-hand sketch shows a concentric-tube simulant, temperatures being taken on the inner tube. More complete details of the designs are given elsewhere.<sup>1</sup>

The copper stretched-skin simulant may be expected to depart somewhat from the performance of a semi-infinite skin or simulant surface because of lateral losses from a system of such small area. Consequently, its performance must be compared experimentally with the results of calculations. The simplest is a bare-skin comparison, corresponding to the calculation of unsteady

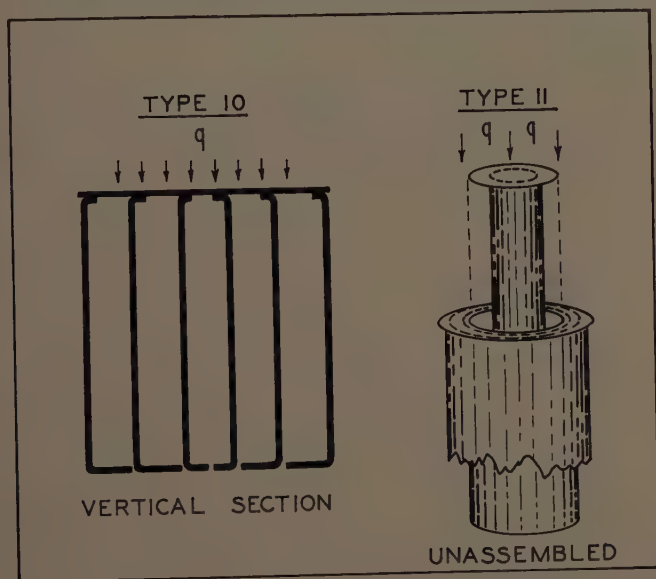


FIGURE 3. Copper simulants.

heat flow in a semi-infinite solid irradiated at a steady rate and losing heat from its surface. FIGURE 4 shows such a comparison, taken from the research of N. Y. Chen.<sup>1, 2</sup> The three dotted lines are calculated temperature-time curves for the skin surface and for two simulated depths below it. The data points, with solid lines through them, are from experiments on three successively better simulants. The first model begins to deviate from theory at about 1 sec., quite probably because of lateral heat flux. The second model stays with theory out to about 5 sec.; the third is in excellent agreement for 12 sec. from initiation of irradiation. Later models, based on type 10 of FIGURE 3, give valid simulation for an even longer time.

*Flux to skin under dry nondecomposing cloth.* The study of heat transfer to skin under dry cloth involves several steps: the formulation of heat flow through an opaque inert layer that is air-spaced from skin, with allowance for external losses; the addition of diathermancy to the cloth property; the development

and testing of a time-saving scheme for building a solution to this more complex problem; and, finally, the testing of the resultant predictions of temperature-time relations at various depths in skin covered with diathermanous cloth.

Conventional formulation of the unsteady heat-flow problem of irradiating a layer of cloth separated from skin by an air layer, with assumption of constancy of all thermal properties during irradiation, yields a relation among the variables indicated in FIGURE 5. The temperature rise (made dimensionless by expression as a ratio to the product of absorbed intensity  $I_o$  and cloth resist-

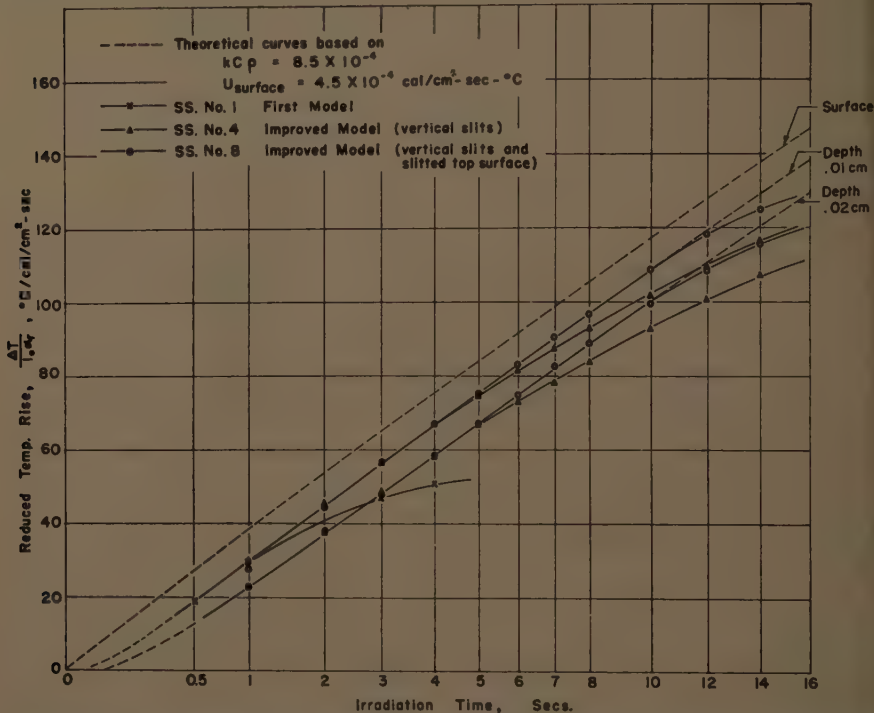


FIGURE 4. Comparison of theoretical performance of a bare-skin simulant with experimental results on three models.

ance  $(L/k)_c$ ) is found to be a function of 5 dimensionless groups representing time, position, external conductance, air-space conductance, and a property group  $R$ , where  $R^2$  equals the ratio of  $kcp$  values for skin and for cloth. For fixed values of the last three groups, expression of the temperature-time-position relation necessitates a family of curves. To make the solution general for a wide range of cloth types and thicknesses and air spaces, Chen's calculations<sup>3</sup> were carried out for each of 4 values of  $U_o$  and each of 4 values of  $U_i$  but a single  $R$ , making 16 families of curves; and a method was developed for allowing for a variation in  $R$  over the range of interest. The results of the calculations, carried out on the Massachusetts Institute of Technology's 704 Computer, appear elsewhere.<sup>3</sup>

The above treatment was inadequate to describe any but dark and tightly woven cloth, however, because of the penetration in depth of radiation; accordingly, the next step was to include allowance for cloth diathermancy. This introduces an additional dimensionless group,  $\gamma L_c$ , where  $\gamma$  is the Beer's-law absorption coefficient and  $L_c$  the cloth thickness. Since a wide range of values of  $\gamma L_c$  is needed to cover all cloth, in principle this multiplies the 16 families of curves by a large number to provide working curves for predictions. An alternative was considered. Let the cloth be divided into two equal slabs. Let the fractions of the total energy transmitted through and absorbed at the skin surface and absorbed in each of the two slabs be calculated, using Beer's law,  $\tau = e^{-\gamma L}$ . Then let it be assumed that the energy, instead of being absorbed continuously in each slab, is absorbed and released for dissipation by conduc-

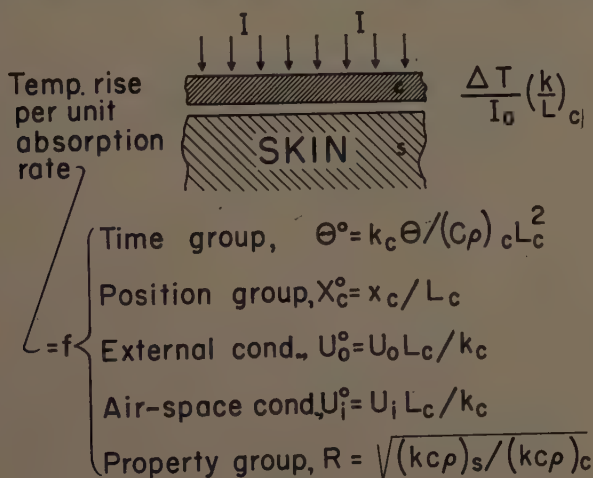


FIGURE 5.

tion at three places: the surface of the skin, in the middle of the second slab, and in the middle or on the surface of the first slab—in the ratios above calculated. Use is then made of the validity of adding solutions of the linear differential equations involved. The temperature rise due independently to heat release at each of the three positions is calculated, and the three solutions are weighted in proportion to the associated heat release and then added. If for the first slab one can assume that the energy is released at the surface rather than at the midplane, the solution is already available in the form of the 16-curve families for the opaque-cloth case; it has been shown that this is generally a better procedure than to assume heat release at the midplane. Two more such families of curves are then necessary, one for the inner slab and one for the skin surface. These have all been calculated on the computer, and the three-curve addition method has been checked for validity against a rigorous treatment of a few special cases. Consequently, there are solutions, available both in tabular and in graphic form,<sup>3</sup> from which one can determine the temperature-time-space pattern in skin under diathermanous cloth of any thick-



ness, diathermancy, surface reflection, and thermal properties, and air-spaced any reasonable distance from the skin.

The relations just described have been tested by experiments using the copper skin simulant overlaid in turn with each of a series of 9-oz. QM standard sateens differing only in color, and ranging from black through grays to white. On each the reflectance and transmittance are available as a function of wave length. Integration over the solar spectrum establishes mean values, and from these one obtains the weighting factors for the three-curve addition method of calculation. The external and air-space conductances  $U_o^\circ$  and  $U_i^\circ$  are not known. The cloth was in contact with the "skin", but other results on opaque cloth had already indicated that cloth nap produced an effective air space of small dimension, failure to allow for which, however, spoiled the agreement with theory. The  $k/L$  of the cloth was also assumed to be unknown. This meant that, in fitting the experimental data on the various cloths to the theory, three parameters could be so chosen as to produce a best fit, but the values for these should be the same for all the cloths, and all should lie within certain known limits. FIGURE 6 shows the experimental data, temperature versus time (normalized) at 4 different depths in the skin, for QM 5 light gray cloth. Superimposed are the theoretical curves for

$$U_o^\circ = 0.1, \quad U_i^\circ = 2, \quad (L/k)_e = 266$$

and for

$$U_o^\circ = 0.09, \quad U_i^\circ = 1.8, \quad (L/k)_e = 240$$

either of which shows remarkable agreement with the data. Furthermore, these same values of parameters fit the data taken on cloths of other colors. The value of  $(k/L)_e$  appears to be established within about 10 per cent, and is probably a more nearly valid value for cloth in use on skin than would be obtained in laboratory steady-state thermal conductivity equipment, where the air space produced by nap would be included in a way improper for unsteady-flow calculations. From literature values for the  $k$  of cotton sateen,  $1.5$  to  $1.8 \times 10^{-4}$ , and from the measured thickness  $L_e$  of  $0.04$  to  $0.045$  cm. for 9 oz. cloth one can deduce that  $L/k$  should lie within the range 220 to 310. The use of  $U_i^\circ (\equiv U_i(L_e/k_e))$  of 2.0 corresponds to a stagnant air layer approximately 0.1 mm. thick, which is reasonable. The use of  $U_o^\circ (\equiv U_o L_e/k_e)$  of 0.1 corresponds to a  $U_o$  of 3 Btu/ft. hr. °F. which is also reasonable, corresponding to convection and radiation coefficients of 2 and 1, respectively. The common best values of  $U_o^\circ$ ,  $U_i^\circ$  and  $k/L$  for all cloth colors and the good agreement of the curve shapes appear to justify the conclusion that the protective value of dry cloth, irradiated at rates below those that produce thermal decomposition sufficient to release heat of combustion or obscuring smoke, can be calculated from theory when the transmittance, reflectance,  $k_e/L_e$  and  $(k\rho)_e$  are known, provided knowledge is available as to the expected mean air gap between cloth and skin in use.

*Flux to skin under moist cloth.* The additional complexities of the heat transfer mechanism when moisture is present have already been touched upon. Particularly distressing is the loss of one prior simplification of great value.

In the dry nondecomposing system a doubling of intensity always doubled the temperature rise, and temperature rise was always additive to whatever starting temperature was used. However, with moisture present the absolute temperature level is of great importance because it determines the vapor pressure, and the  $\Delta T$  due to moisture is not linear in intensity.

This can be only a preliminary progress report on the moisture problem. What has been done<sup>2</sup> is to make the following assumptions concerning the way

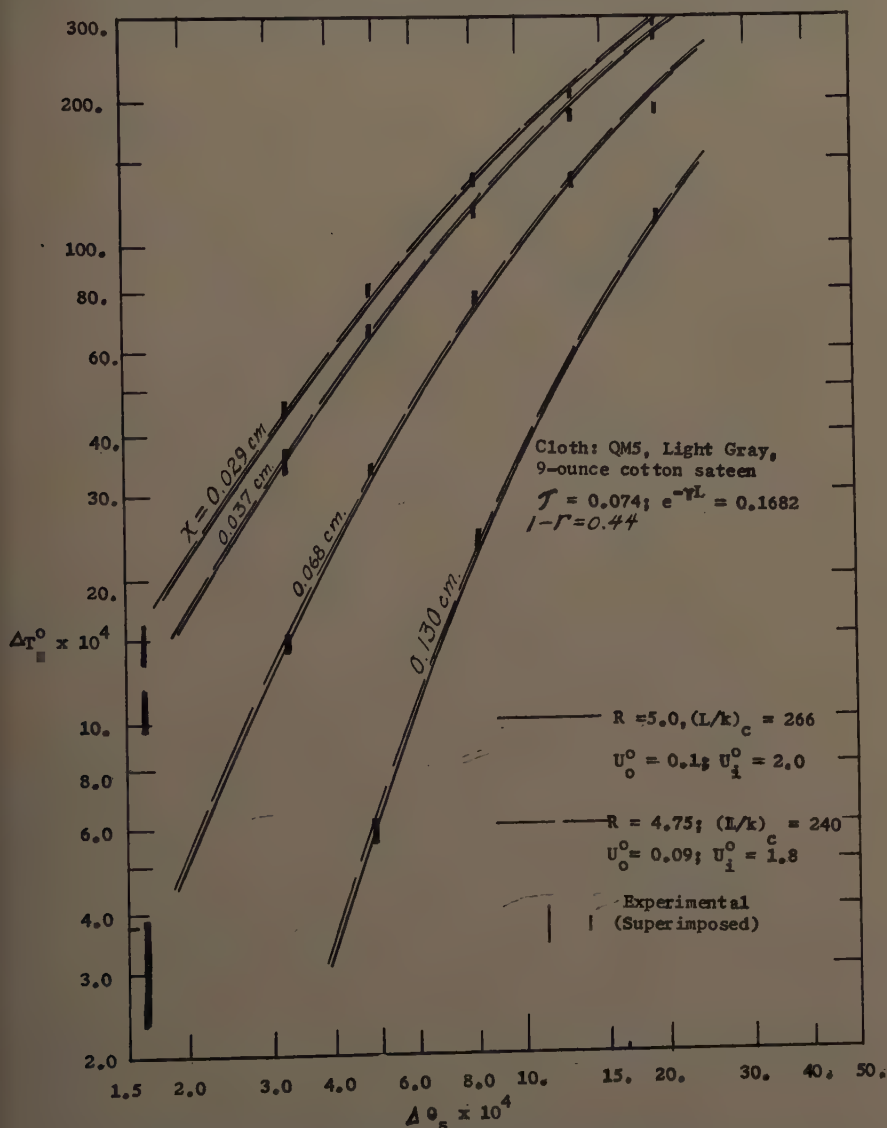


FIGURE 6. Comparison of theoretical and experimental temperature histories within a skin simulant following thermal irradiation through overlying diathermanous cloth.

moisture moves in irradiated cloth: (1) the equilibrium fiber moisture content is known as a function of air temperature and humidity; (2) the moisture in the air around individual cloth microfibers is in equilibrium with the fiber moisture content; and (3) the movement of moisture in the cloth is by vapor-phase diffusion through the air.

FIGURE 7 serves to delineate the problem. The cumulative incident energy versus time, for steady irradiation, appears as a straight line through the origin. Outward losses modify the absorbed energy and produce downward curvature at the upper end of the line. The other heavy line, marked  $Q_2$ , shows the

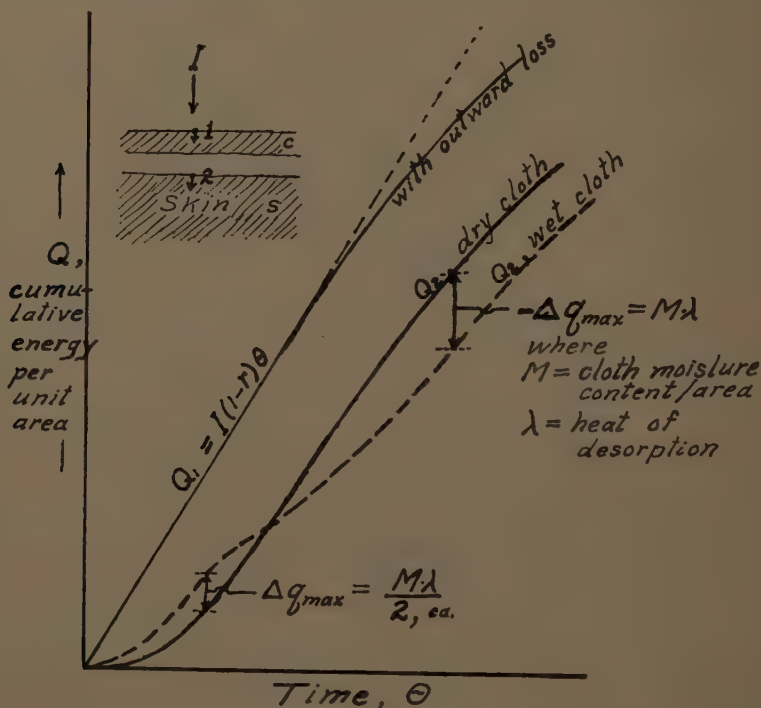


FIGURE 7.

cumulative flux of energy through the surface of skin under dry cloth. The dashed line (qualitative) represents the corresponding flux through the skin surface when the cloth is moist. At first the moisture moves from the outer surface of irradiated cloth in two directions, some toward the skin and some toward the outer air and, if about one half moves each way, the dashed curve will lie above the dry-cloth curve, at some period early in the irradiation, by an amount equal to perhaps one half the energy of desorption of the cloth moisture. If the resultant flux up to this point is harmful, the presence of moisture will have produced an undesirable speed-up in heat transfer. For longer irradiation times, however, the moisture initially driven in by the heat wave starts back out and the result is that, for long-time irradiation, the total energy absorbed at the skin is less than that for the dry-cloth case by an amount equal



to the heat of desorption of the total cloth moisture initially present. If the irradiation density is so low that long-time irradiation is necessary to produce damage, the effect of cloth moisture is seen to be beneficial.

Preliminary quantitative comparisons of theory with experiment are shown in FIGURE 8, where the temperature rise is plotted versus depth below skin surface for each of several irradiation times and for both dry and wet cloth. The

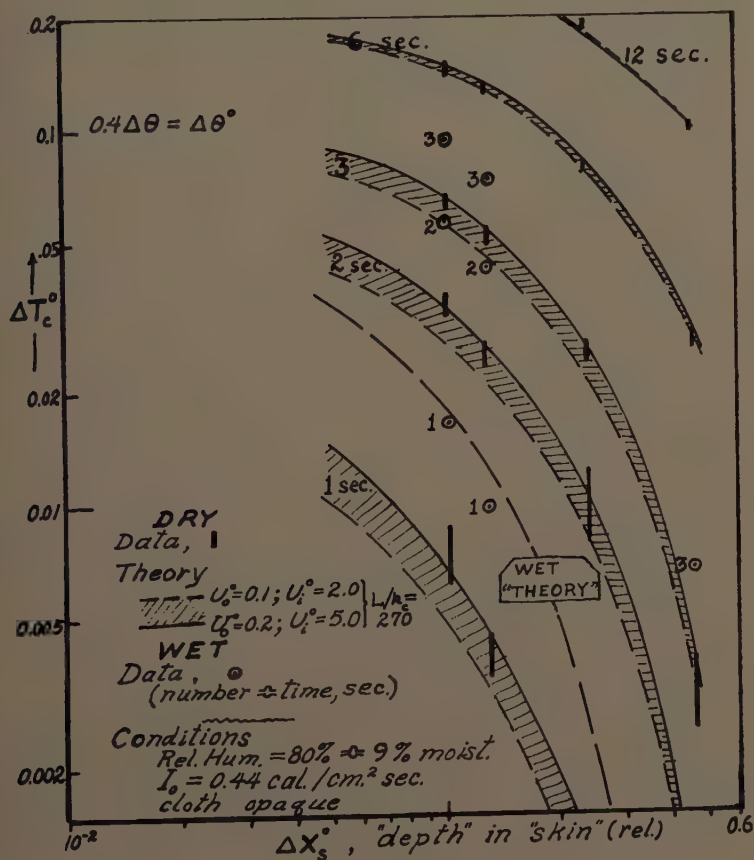


FIGURE 8.

data on wet cloth at one second are seen to lie encouragingly close to the calculated curve. The calculations for 2 and 3 sec., wet cloth, have not been completed; the data indicate that the skin temperature rise is higher than under dry cloth. This work is continuing.

It may be concluded that the theory of heat and moisture transfer through thermally irradiated cloth onto skin is moderately well developed, although some factors that enter when the irradiation density is quite high have not been included. It is hoped that allowance can be made for these factors, particularly bulk movement of moisture and thermal decomposition of the cloth,

and that the resultant quantitative understanding of the process may aid in the development of protective clothing of improved characteristics.

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## CLOTHING PROTECTION IN MODERN WARFARE

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### *Introduction*

The Quartermaster Corps (QMC) has primary responsibility for the United States Army for research and development of protective clothing and protective accessories. This includes not only protection against the environment, but also against ballistic, CBR, and thermal hazards.

During World War II and the Korean conflict separate new items were provided as new forms of protection were required. However, with the increase in the number of potential battle stresses, it will be impossible to continue to provide separate types of protection. The number of different protective items each soldier would require at one time would be of a fairly large magnitude. It would be difficult to insure that each soldier would have the appropriate form of protection at the right place at the right time. The logistic support problem would be tremendous.

The QMC is presently attempting to combine into a single clothing system the maximum attainable protection to enable the soldier to perform his task without an insupportable logistic burden. This is a major mission of the Quartermaster Research and Engineering Command (QMREC), Natick, Mass.

Here, however, we shall concern ourselves with only one aspect of this combined protective system; namely, protection against the thermal effects of nuclear weapons.

With the advent of nuclear weapons, the soldier became subject to two new battlefield hazards, thermal and ionizing radiation. Although flame-type weapons had been used in warfare previously, thermal radiation as such had little or no major casualty-producing potential. Nuclear weapons have drastically changed this picture and thermal radiation is now a serious hazard. It has been estimated that 20 to 30 per cent of the fatal casualties resulting from the atomic bombings of Japan were due to flash burns; it has also been estimated that from 60 to 80 per cent of the survivors suffered flash burns.

For a 20 KT weapon fatal injuries from blast, burns, and/or nuclear radiation can result within a radius of about 4000 feet from ground zero. Burns can be expected when unprotected skin is exposed to about 3 cal./cm.<sup>2</sup> of thermal radiant energy delivered in 1 second or less, out to about 12,000 feet from ground zero. When the skin is covered with summer-weight clothing, the hazard of burns becomes more pronounced within the 4,000 to 12,000 foot radii from ground zero if there is ignition of such clothing. As the yield of the weapons increases, the ground area for incapacitating burns also increases.

The QMREC is presently engaged in a program whose objective is to provide thermal protection for the individual soldier and his clothing against certain levels of radiant energy of a classified nature.

The QMC work in the thermal field began about 1943. It was concerned chiefly with the flameproofing of clothing. This work was enlarged to include the effects of thermal radiation about 1952.

A good deal of work in the evaluation of materials, systems, and designs has been undertaken and accomplished in the laboratory. In addition, the command has participated in a number of field trials in both Nevada and the Pacific, where materials and systems have been exposed to actual atomic detonations.

When the thermal project commenced, clothing in the supply system was evaluated for thermal protection. It was determined that the cold-weather clothing, both for cold-dry and the cold-wet areas, provided adequate thermal protection according to the Department of the Army (D/A) requirements set down for this project. It was also established that, in order to prevent flaming, fire-retardant-treated fabrics were of definite benefit.

There is good agreement among investigators who have studied the thermal problem that bare-skin areas such as the hands, face, and neck present an extremely critical problem. This problem is pointed up in a recent article by Langevin *et al.* in a recent study on "Effectiveness of Troops Exposed to Thermal Radiation from Nuclear Weapons."<sup>1</sup> There appears, however, to be a misconception in some quarters that summer-weight (hot-weather) clothing will afford the wearer up to 20 cal./cm.<sup>2</sup> protection. Our laboratory work and field tests in 1953 and 1957 have demonstrated that thermal protection afforded by hot-weather clothing falls far below this level.

#### *Hot-Weather Uniforms*

In hot-weather areas, we are attempting to keep the men as comfortable as possible by means of lightweight clothing. At the same time we are trying to provide thermal protection that would require, at present, as much material as is used for cold-weather clothing. One method of overcoming these contradictory requirements is by the use of a space between layers of clothing for increased thermal protection. It has been discovered that fabrics, when spaced away from the skin, give better protection than when the clothing is in direct contact. It has also been determined that flaming fabric may cause a much more severe insult to the skin than radiant thermal energy alone. As a result, an experimental hot-weather ensemble has been developed that will provide thermal protection approximating our minimum requirement. This ensemble is relatively lightweight. It utilizes the spacing principle between layers of clothing, and has a flame-retardant treatment on the outer fabric layer. This ensemble consists of three layers: (1) an outer layer of cotton, poplin, 5 oz./yd.<sup>2</sup> that is fire-retardant, having been treated with tetrakis(hydroxymethyl) phosphonium chloride (THPC); (2) an intermediate spacer material made from cloth, a heat-set polyethylene leno weave that provides approximately one-quarter-inch spacing; and (3) an inner layer of T-shirt material (cotton, tubular knit, 3.2 oz./yd.<sup>2</sup>).

Tests were carried out in Nevada in which this experimental ensemble was fabricated into animal uniforms and placed on anesthetized pigs at varying distances from ground zero. At these same distances from ground zero, other pigs dressed in regular summer-weight uniforms consisting of a two-layer system of a nonfire-retardant outer layer of poplin and an inner layer of T-shirt material in contact were employed as controls. The experimental uniform at



each distance gave much better protection than that provided by the control uniform. The superior protection provided by the experimental uniforms was evidenced by only mild burns or the complete lack of burns experienced by the animals, as compared to the much more severe burns experienced by the animals wearing the control uniforms.

In spite of the fact that a uniform system may give a degree of thermal protection to the wearer, another problem is posed in every instance where this occurs. The problem is the destruction of the outer layer of the uniform. The individual with a destroyed outer layer of uniform is not protected against future thermal insults and is also not protected against the particular environment in which he is at the time. In addition, a logistic problem of varying degrees of magnitude is presented to the supply arm of the military services.

The thermal project, at present, is investigating the possibility of developing synthetic materials that will withstand the thermal energies of interest without degradation and, at the same time, provide thermal protection. This work is in the feasibility stage, and there is nothing of an unclassified nature to report at this time.

### *Protection for Bare-Skin Areas*

During World War II a cream was developed by the Navy to protect normally bare-skin areas of gunners against flash burns encountered in naval warfare. As a result of the introduction of nuclear warfare, better thermal protection for all personnel is required. To provide such protection, especially for the face, research and development of spreadable creams were initiated at the QMREC.

To be satisfactory, a cream must: (1) provide the required degree of thermal protection; (2) be acceptable to the wearer; (3) be durable; (4) be nontoxic and nonirritating; (5) not rub or peel off; and (6) not interfere with a soldier's combat activities. The first and foremost requisite is that the cream must provide the required thermal protection. Still, in the development of a cream, the other requirements must always be kept in mind. To meet the physical characteristics cosmetically, a cream must contain certain basic types of ingredients such as film formers to give it abrasion resistance; tackifiers, so that it will adhere to the skin; emulsifying agents to promote the formation of a homogeneous mixture; and plasticizers to give it flexibility.

Two general types of formulations have been studied: oil-base and water-base creams. Two experimental creams have been developed that provide adequate thermal protection; one is an oil-base and the other a water-base cream. The oil base is the better of the two from a wearability standpoint under simulated combat conditions. The oil-based creams have been tested on animals exposed to actual nuclear detonations in Nevada. This cream has also had limited testing on troops under simulated combat conditions, and appears to be acceptable for limited use.

This cream contains the following ingredients: methyl cellulose, chlorinated paraffin, titanium dioxide, magnesium carbonate, ferric oxide, water, stearic acid, calcium stearate, and hydroabietyl alcohol.

To be effective as a thermal barrier, this cream must be applied to the skin

in a thickness of one-sixteenth of an inch. It is planned to present this cream to the Continental Army Command (CONARC), Fort Monroe, Va., during 1959 as an interim protective thermal cream.

In working with these creams, the alcohol in one case was replaced by carbon tetrachloride for the purpose of reducing flammability. An exposure of one-sixteenth-inch layer of this cream on an inanimate receiver (transite) at 21.6 cal./cm.<sup>2</sup> for one second produced no temperature rise at the cream transite interface. When the exposure period was extended to 5 sec., corresponding to a total energy of 108 calories, the temperature rise was only 23.7° C. As a result of this preliminary work, formulations using various types of organic chemicals have been developed. The thermal protective qualities of some of these compounds are phenomenal. For example, one-sixteenth inch of one of these formulations on exposure to 137 cal./cm.<sup>2</sup> delivered at the rate of 27.4 cal./cm.<sup>2</sup> for 5 sec. afforded complete protection to the skin of pigs. Indications from laboratory results are that protection can be effected up to 400 cal./cm.<sup>2</sup> delivered in 20 sec.

The mechanism responsible for these thermal protective properties is not known at present. However, basic work is being carried on in our laboratories now to determine what these properties are. Much more significant than the immediate explanation of this phenomenon is the fact that these findings suggest an approach to the development of thermal barrier materials that will be effective against the larger thermal pulse of thermonuclear weapons.

#### *Effect of Short Versus Long Thermal Pulses*

Quite frequently statements are made to the effect that a given quantity of thermal energy from a higher-yield weapon is less severe than the same amount from a lower-yield weapon. Except for very low orders of irradiance, we have not found or seen any evidence to support this statement with respect to clothing. For example, if one excludes the potential for taking evasive action, it will require less clothing to protect a man against 30 cal./cm.<sup>2</sup> delivered in 0.5 sec. than to afford him equal protection against 10 cal./cm.<sup>2</sup>/sec. for 3 sec.

#### *Solar Furnace*

As far back as 1951, 1952, and 1953, when the QMC participated in the Pacific and Nevada atomic tests, it became apparent that there was a real need for a laboratory source that would yield a high thermal flux over a much larger area than that obtainable with a carbon arc. To date, the principal sources used to simulate the thermal effects of nuclear weapons have been the carbon arc and magnesium flash powder. Both have serious deficiencies. The area of irradiation from the QM carbon arc is limited to a maximum of about a one-half-inch diameter circle with an energy flux of approximately 30 cal./cm.<sup>2</sup>/sec. Magnesium flash powder is difficult to control and lacks desired spectral characteristics. As a result of the inadequacy of these sources, the QMREC constructed a solar furnace that was dedicated on September 30, 1958. This furnace has been designed primarily for, but not limited to, laboratory testing of QM materials for protection of the soldier against thermal effects of nuclear and other weapons. It is capable of producing a thermal flux in excess of 60 cal./cm.<sup>2</sup>/sec. over an area 4 inches in diameter.

Four major components make up the solar furnace: heliostat, concentrator, attenuator, and test chamber (FIGURE 1).

The heliostat is 40 feet long and 36 feet high, and bears 356 optically adjusted mirrors comprising a single reflecting surface. Its basic requirement is to maintain fixed parallel beams of reflected sunlight by "tracking" the sun onto the concentrator, 96 feet distant. Because of its great latitude of adjustability, the heliostat can obtain usable solar radiation for the greater part of a normally clear day. Its lakeside site also furnishes an extended horizon.

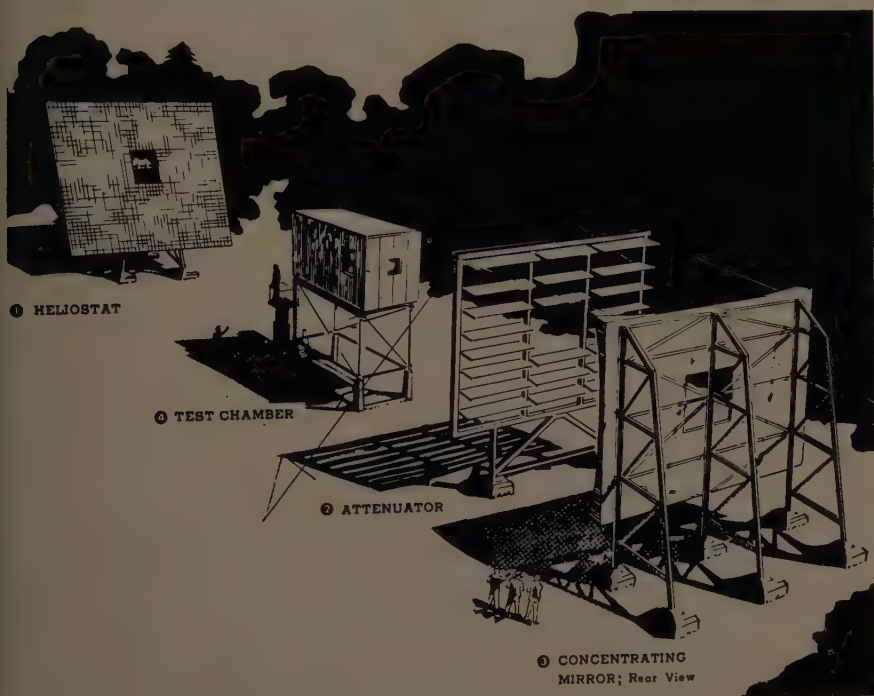


FIGURE 1.

One hundred and eighty concave, rectangular mirrors comprise the concentrator surface, itself spherical in contour. Each mirror is individually adjusted so that a convergent, tremendously intensified beam is created and focused into the four-inch test area within the test chamber. Use of multiple spherical mirrors was found to offer great dollar savings over the traditional continuous surface mirror.

The attenuator, controlling the "feeding" of solar radiation to the concentrator through its 17 lateral shutters, also serves as a safety mechanism, closing automatically in case of overradiation or power failure.

All controls and the laboratory testing equipment are housed in the test chamber which, with its 8-foot-square face and 16-foot length, matches the apertures centered in the concentrator and attenuator. About 2 feet inside the test chamber window is the focal point of the built-up solar radiation.

There materials under test may be subjected to shutter-controlled exposures of high or low thermal flux. The radiation from this device closely simulates the thermal radiation that would be received by materials or personnel in the vicinity of nuclear weapon detonations.

### *Summary*

The critical problems that remain unsolved in the thermal protection of the individual soldier are: bare-skin areas, that is, the hands, face and neck; and hot-weather clothing. Potential approaches to these problems that offer good possibilities for success include hand and face creams and face masks; fire-retardant fabrics or fibers with spacer systems that hold the clothing away from the body; fire-retardant fibers or fabrics that will remain intact for several seconds even though burned to a state of char; and the incorporation of high-energy dissipating compounds into face creams or fabrics. As indicated earlier, such compounds have been discovered in our laboratories. The problem is to determine the mechanism by which they function and to find a means of utilizing them effectively.

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# THE EFFECTS OF THERMAL RADIATION ON MATERIALS

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## *Introduction*

When radiation falls on matter, part will be reflected, part will be transmitted through the material, and the remainder will be absorbed. The extent of the absorption of radiation by a material depends on the nature of the material and its color. Some of the radiation absorbed, particularly that in the ultraviolet spectral region, may produce chemical reaction, but most of the absorbed radiation is converted directly into heat. As a consequence, the temperature of the absorbing material rises, and damage may result. If the radiant energy is delivered in a very short time the intensity of the radiation, or irradiance, is very high. Because of this high irradiance, the heat accompanying the absorption of thermal radiation is produced rapidly, most of it in the surface of the body upon which it falls. Since only a small proportion of the heat is dissipated by conduction during the short interval, high surface temperatures are attained. If the emission and absorption of the same amount of thermal radiation should occur over a much longer period, the surface temperatures may be considerably lower, and the consequent damage much less, although the total amounts of radiation absorbed and of heat produced would be unchanged.

One of the most important physical effects of the high temperatures due to the absorption of thermal radiation is, of course, ignition or charring of combustible materials. The ignition of materials involves a large number of factors and, in general, it is very difficult to establish definite conditions under which such burning will or will not occur. In the earliest considerations of the effects of atomic detonations it was assumed that if the heat is supplied at a rapid rate, as would be the case for the absorption of very intense radiation, the essential criterion would be the total energy received per unit area. It would appear that, as the rate of heat supply increases, the total energy necessary to produce charring at first decreases, and then reaches a constant value. This means that, assuming the heat to be supplied sufficiently rapidly, as it is by the thermal radiation from an atomic bomb burst, there is a certain minimum or critical quantity of heat energy per unit area, the "critical energy" or "critical radiant exposure," which is necessary to produce thermal damage in materials. Under these conditions, "reciprocity" is said to hold. Reciprocity, however, may not necessarily hold, particularly for the longer exposure times, for several reasons, such as losses due to reradiation, obscuration by smoke and combustion products expelled from the surface of the irradiated cloth, and changes in the cloth's reflectance during the irradiation period.

The earliest laboratory studies on the effects of thermal radiation on materials involved exposures in which the irradiance either was constant during the exposure period or varied according to a Gaussian distribution. Until sufficient data were obtained on the variation of radiant flux with time for the various

operational weapons, it was considered possible to equate exposures to the field pulse with corresponding exposures to a single equivalent constant-irradiance laboratory source. A laboratory source has since been developed and constructed at the Naval Material Laboratory in which the intensity of irradiation varies with time in a manner similar to that of the "generalized" field pulse.

The purpose of this study was to measure the radiant exposures required to produce thermal damage in cloths as a function of the time of exposure to thermal radiation for both constant-irradiance pulses and for simulated nuclear weapon pulses.

### *Damage Criteria*

Three critical damage points on the cloths were studied: (1) threshold, or the point of incipient damage; (2) char-through, the point at which the back surface is initially charred; and (3) destruction, the point at which the specimen is consumed either by the radiation or by self-sustained burning.

Threshold scorch is a gradual effect involving, for relatively low radiant exposures, only a few isolated fibers, and more and more fibers as the thermal flux is increased; considerable judgment is required in determining the actual degree of scorch, and errors among independently trained observers might be as large as 10 per cent. In the case of the darker cloths, threshold scorch, generally characterized as browning, is difficult to discern and relatively higher radiant energies are required to produce a visible scorch. It was noted in the course of these experiments that, while threshold scorch occurred only on the surface for the shorter exposures, it extended through the fabric for the longer exposures. Threshold destruction of the cotton fabrics was associated with glow that was initiated in a spot in the center of the exposed area and consumed the cloth some seconds after the exposure was terminated. Threshold destruction of the wool fabrics was defined as the coalescing or distortion of the fabrics, since this effect occurred long before the cloth material was consumed.

### *Sources of Radiation*

The three principal sources of radiation employed in the NML Thermal Radiation studies all utilize a carbon-arc source and reflecting optics. The first source (FIGURE 1) utilizes standard 11-mm. high-intensity searchlight carbons, with an ellipsoidal reflector whose primary and secondary foci are 11 and 55 inches, respectively. The source is placed at the primary focus and the target material is irradiated at the secondary focus. The radiation converges in a solid angle of  $30^\circ$ . The intensity of irradiation, or irradiance, is reasonably uniform over an area 17 mm. in diameter; the irradiance profile is approximately Gaussian. The irradiance falls to 90 per cent of its maximum value at 6 mm. from the center. A twin-bladed solenoid-driven shutter with a transit time of 10 msec. provides essentially rectangular pulses. Thermal damage to an irradiated cloth is essentially uniform over an area 5 mm. in diameter in the center of the irradiated area; for this reason, a 5-mm. aperture is placed over the calorimeter for determining the irradiance effective in producing damage. With high-intensity carbons the maximum irradiance obtainable is 18 cal./cm.<sup>2</sup> sec.; with National Carbon's Ultrex carbons the maximum irradi-

ance is 30 cal./cm.<sup>2</sup> sec. A series of perforated metal screens was employed to adjust the irradiance to the desired value.

The second source (FIGURE 2) utilizes the energy emitted by a 16-mm. carbon, a paraboloidal reflector collimating the energy and a similar reflector, at a distance of 20 feet, condensing the energy onto the material at the focus of

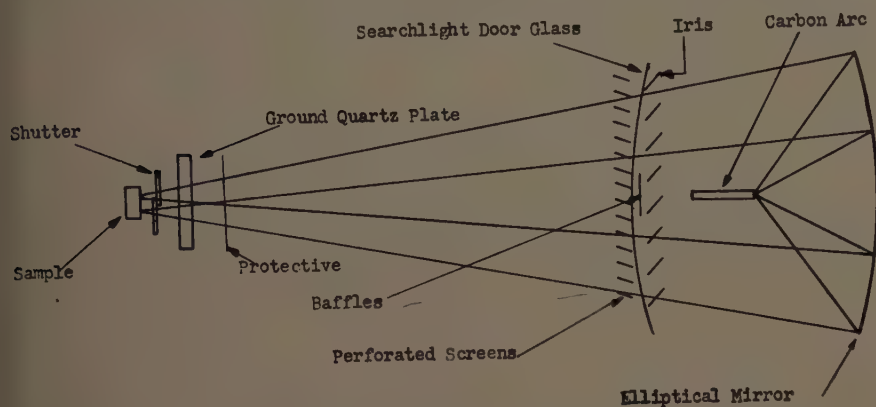


FIGURE 1. NML 24-inch ellipsoidal mirror arc-image source of thermal radiation.

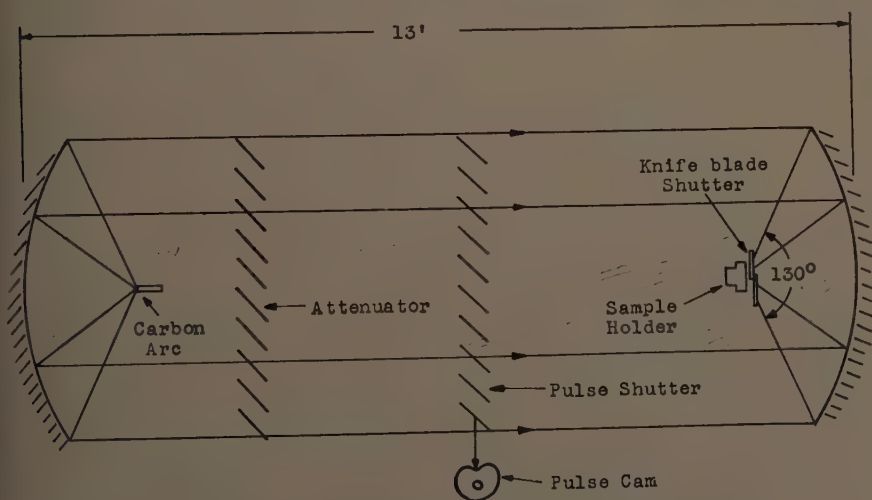


FIGURE 2. NML 36-inch paraboloidal mirror arc-image source of thermal radiation.

the condensing mirror. A maximum irradiance of 100 cal./cm.<sup>2</sup> sec. is obtained, but the irradiance at the target is uniform only in the central area, 9 mm. in diameter.

The third source (FIGURE 3) is similar to the second, but employs 11-mm. carbons. Whereas the first two sources utilize fast-acting shutters mounted directly in front of the sample, in the third source the target is mounted on a carriage moving transversely to the axis of the reflector and through the focus.



The irradiance distribution is essentially Gaussian, with a maximum value of 85 cal./cm.<sup>2</sup>sec. over a central area, which is 2 mm. wide. The critical radiant exposure  $Q_c$  for these exposures has been determined from the relationship

$$Q_c = H_o t_w$$

where  $H_o$  is the peak irradiance and  $t_w$  is the duration of the equivalent rectangular pulse, that is, the duration for which the pulse would have to be given if it were all given at the maximum rate. It can be shown that

$$H_t = 87 \exp [-\pi(86/Q_c)^2(t - t_o)^2] \text{ cal./cm.}^2\text{sec.}$$

where  $H_t$  is the irradiance at time  $t$ ,  $Q_c$  the critical radiant exposure for the

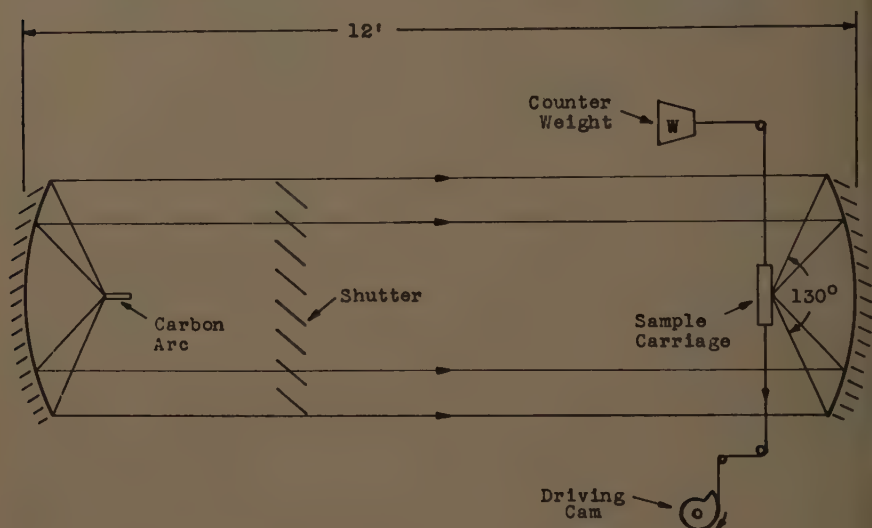


FIGURE 3. NML 24-inch paraboloidal mirror arc-image source of thermal radiation.

particular damage level, is equal to  $83/v$ , where  $v$  is the velocity of the target sample as that particular area passes through the irradiated area.

### *Experimental Procedure*

In the experiments reported in this paper, the cloths, cut into convenient pieces and preconditioned to the desired moisture content, were irradiated in a sequence of exposures with durations increasing in increments of approximately 10 per cent. When a certain effect of particular interest was noted, exposures were repeated until it was estimated that the radiant exposure to cause the particular effect was known to within 10 per cent.

### *Correlation of Sources*

The critical thermal energies required to produce a given level of damage by exposure to the dynamic-exposure source and to the 9-mm.-static-exposure source were correlated with the critical thermal energy required to produce the same level of damage by exposure to the 17-mm.-static-exposure source.

The radiant exposures for threshold damage, char-through, and destruction for a given exposure time,  $t$ , were correlated, using the general relationship

$$Q_c' = kQ_c t^a \quad (1)$$

where  $Q_c'$  refers to the radiant exposure for the dynamic-exposure source or that for the 9-mm. static-exposure source.  $Q_c$  refers to the data for the 17-mm. static-exposure source, and  $k$  and  $a$  are empirical constants, which are given in TABLE 1.

### *The Thermal Radiation of Nuclear Detonations*

The results of numerous field tests have shown that the ball of fire in a nuclear detonation does not behave as a perfect radiator. This is due to a number of factors. The surface temperature during the first radiation pulse is modified by the disturbed air immediately around the fireball and, at later times, the temperature is not that of the surface, but the result of radiation some distance within the fireball. The radius of the fireball during the second

TABLE 1  
CORRELATION OF RADIANT EXPOSURES TO LABORATORY SOURCES  
DAMAGE TO FABRICS

Damage	Source	$k$	$a$
Threshold	dynamic exposure	1.74	0.13
	9-mm. static exposure	1.12	0.00
Char-through	dynamic exposure	1.32	0.00
	9-mm. static exposure	0.97	0.00
Destruction	dynamic exposure	0.96	0.33
	9-mm. static exposure	1.35	-0.10

thermal pulse is very difficult to determine because the surface of the luminous fireball becomes very diffuse. Since the radii and surface temperatures will depend on the energy yield of the explosion, a different curve will be obtained for every value of the yield. However, it is possible to generalize the results by means of scaling laws, so that a curve applicable to the second pulse for all energy yields can be obtained from a single set of calculations. Actually, the power  $P$  is measured directly as a function of time  $t$  for each explosion. However, instead of plotting  $P$  versus  $t$ , a curve is drawn of the scaled power, that is,  $P/P_{\max}$  versus the scaled time  $t/t_{\max}$ , where  $P_{\max}$  is the maximum value of the thermal power, corresponding to the temperature maximum in the second pulse, and  $t_{\max}$  is the time at which this maximum is attained. The resulting curve, shown in FIGURE 4, is of general applicability, irrespective of the yield of the explosion. Also shown in FIGURE 4 is the irradiance-time characteristic of the 17-mm.static-exposure source, which results from the modulation of the radiation by a cam-driven radial-vane shutter.

### *Physical Characteristics of Cloths*

The physical constants of the six cloths employed in this study are listed in TABLE 2. After cutting the cloths into  $2\frac{1}{2} \times 3$ -inch strips, each test sample

was conditioned according to a schedule employed in most fabric testing laboratories. The procedure entails heating the cloth in an oven at 105° C. for 1 hour to drive off any water, then keeping it for at least 24 hours in a chamber at 20° C. and 65 per cent relative humidity, and then subjecting it to the intense thermal radiation according to the test plan.

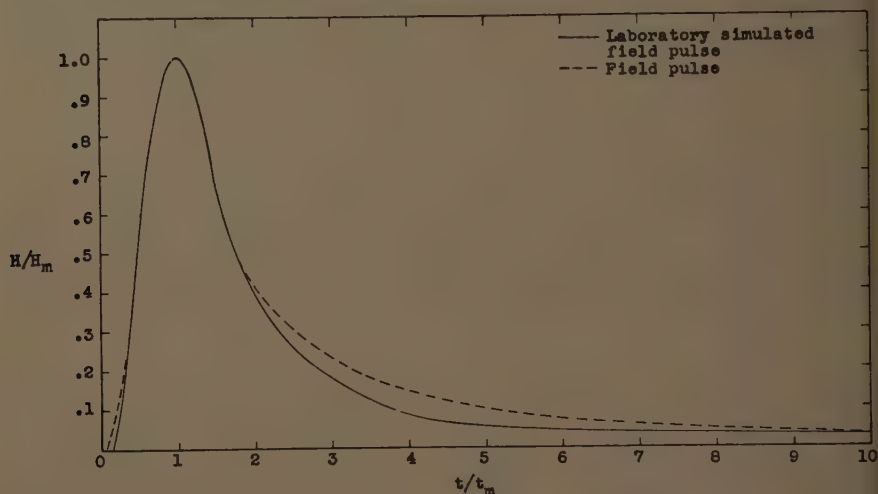


FIGURE 4. Laboratory replication of generalized field pulse.

TABLE 2  
PHYSICAL CHARACTERISTICS OF CLOTHS

Cloth Description	Weight (oz./yd. <sup>2</sup> )	Thickness (cm.)	Carbon- arc reflectance	Carbon-arc transmittance	Diathermancy (cm. <sup>-1</sup> )
Cotton denim, blue; dungaree	9	0.071	0.35	0.03	43
Cotton twill, khaki; shirt, tropical	5.2	0.031	0.53	0.11	46
Wool gabardine, gray; shirt	7.7	0.050	0.54	0.16	22
Cotton chambray, blue, work shirt	2.9	0.024	0.47	0.20	40
Cotton sateen, OG107	9.0	0.045	0.31	0.02	95
Cotton twill, light gray	7.7	0.059	0.51	0.10	30.8
Cotton twill, black	7.8	0.056	0.75	0.03	81
Cotton oxford, OG-107, water repellant	5.5	0.027	0.30	0.07	140
Wool serge, white	5.6	0.042	0.44	0.26	19
Wool serge, white	11.2	0.081	0.44	0.16	19

The spectral reflectance and transmittance of the cloths were measured, employing the Perkin-Elmer Infrared Spectrometer and a recording reflectometer designed and constructed by the Naval Material Laboratory, both instruments having quartz optics. The effective total reflectance and transmittance for the carbon-arc spectrum was computed. The effective diathermancy of each cloth was determined from the expression

$$\gamma = \frac{1}{l} \log_e \left( \frac{1 - R}{T} \right)$$

where  $l$  is the measured thickness.



*Thermal Damage as a Function of Exposure Time, Constant-Irradiance Pulses*

The critical radiant exposures required to cause thermal damage to the cloths are given in TABLE 3 for the three damage levels and the various exposure times investigated. The data are for constant-irradiance exposures to the 17-mm. static-exposure source; where data for this source were lacking, because the maximum irradiance obtainable with this source was inadequate, as at the shorter exposure times, the data for the exposures to the other sources were modified, using EQUATION 1 and the constants given in TABLE 1.

The critical radiant exposures corresponding to threshold damage, char-through, and destruction are given in FIGURES 5, 6, and 7, respectively, as a function of the time of exposure. The radiant exposures are given in terms of

TABLE 3  
RADIANT EXPOSURE REQUIRED TO DAMAGE CLOTHS AS A FUNCTION OF TIME OF EXPOSURE, RECTANGULAR PULSES

Cloth	Damage	Radiant exposure (cal./cm. <sup>2</sup> )									
		Time of exposure (sec.)									
		0.1	0.2	0.3	0.5	1.0	3.0	10.0	20.0	30.0	60.0
Cotton sateen, OG-107, 9 oz./yd. <sup>2</sup>	Threshold	1.8	2.7	4.2	4.8	5.7	8.3	11.0	13.0	18.5	
	Char-through	6.5	5.0	5.5	6.0	7.0	9.0	13.2	17.5	22.0	
	Destruction		9.0	9.0	9.0	9.8	12.0	16.5	21.0	24.5	39.0
Cotton, twill, light gray 7.7 oz./yd. <sup>2</sup>	Threshold	5.0	4.9	5.5	6.5	8.0	11.0	14.0	18.0	23.0	
	Char-through		8.5	9.3	10.0	11.0	13.0	16.5	21.0	24.0	
	Destruction			12.0	12.0	12.0	14.8	24.0			
Cotton, twill, black 7.8 oz./yd. <sup>2</sup>	Threshold	1.3	1.6	3.0	3.8	5.0	7.5	11.3	14.0		
	Char-through		6.5	5.0	6.8	7.0	8.5	13.0	16.0		
	Destruction		14.0	11.5	10.0	9.0	11.0	15.0	20.0		
Cotton, oxford, OG-107 5.5 oz./yd. <sup>2</sup> , water-repellant	Threshold	4.9	4.9	4.9	4.9	4.9	6.1	11.0	15.5	20.0	
	Char-through	8.0	6.5	6.5	6.5	6.5	7.5	11.0	15.5	20.0	
	Destruction	10.0	10.0	10.0	10.0	10.5	12.0	16.5			
Wool, serge, white, 5.6 oz./yd. <sup>2</sup>	Threshold	4.7	4.8	5.0	6.5	8.0	11.0	13.3	16.0	21.8	
	Char-through		10.0	10.0	10.5	9.0	14.0	20.0	17.0		
	Destruction		9.5	9.5	9.5	12.5	18.3	28.0			
Wool, serge, white 11.2 oz./yd. <sup>2</sup>	Threshold	4.6	7.6	8.2	9.0	9.3	11.5	15.0	18.5	22.0	30.0
	Char-through										
	Destruction				29.0	25.0	27.0	44.0			

the radiant exposure for a rectangular pulse of 1 sec. There is no consistent trend among the data for each individual cloth but, if each point is considered statistically independent, there appears to be a regular relationship between the radiant exposure and exposure time, namely

$$Q = Q_{1.0} t^b$$

where  $Q$  is the radiant exposure for time  $t$ ;  $Q_{1.0}$  is the radiant exposure for a 1.0-sec. pulse; and  $b$  is an empirical constant, as given in TABLE 4.

*Thermal Damage to Fabrics for Nuclear Weapon Pulses*

The radiant exposures that cause various levels of thermal damage were determined for the laboratory pulse that approximates the generalized field pulse. For purposes of comparison, a series of measurements was made, employing constant-irradiance exposures.

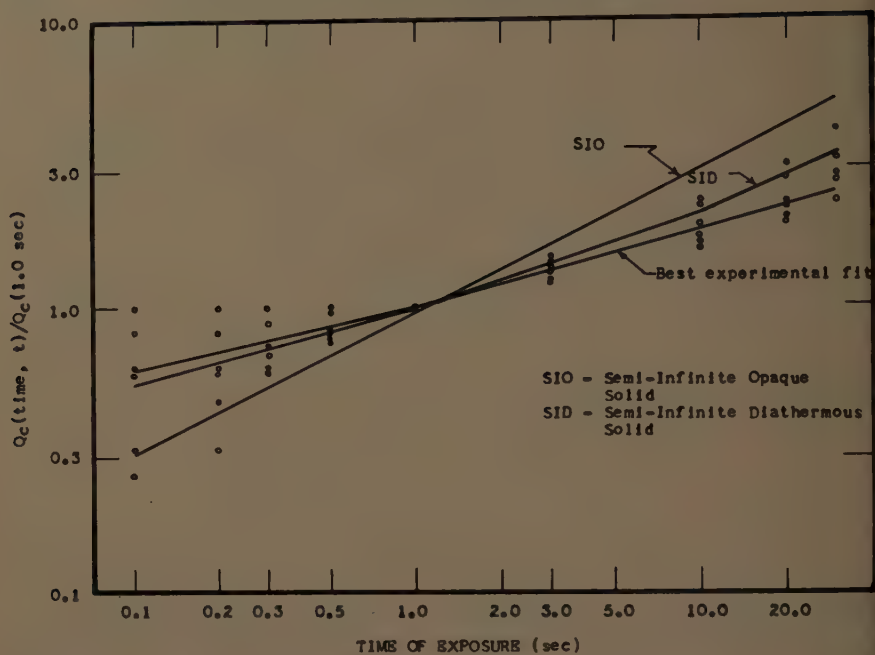


FIGURE 5. Critical radiant exposure corresponding to threshold damage of cloths as a function of time of exposure.

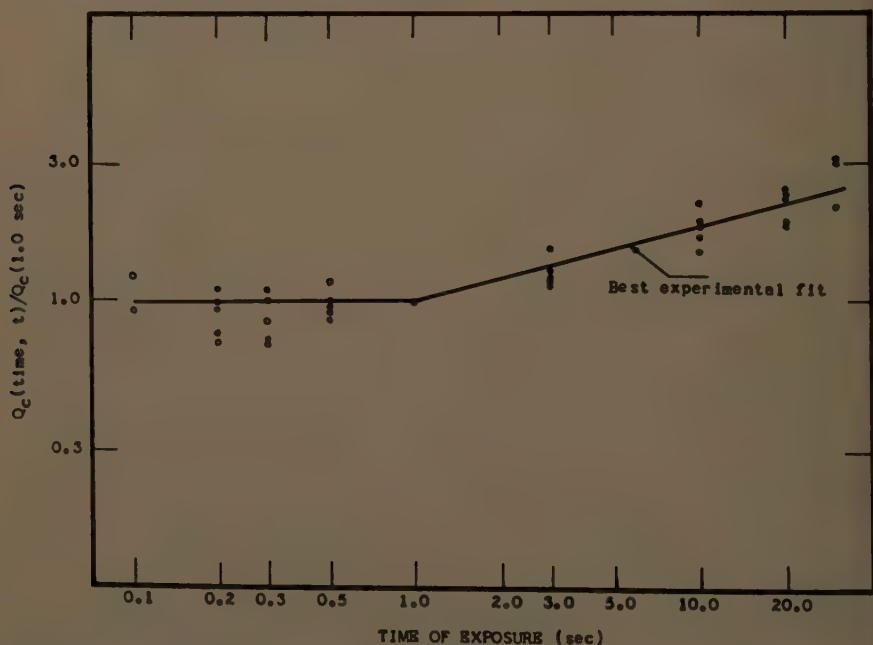


FIGURE 6. Critical radiant exposure corresponding to char-through of cloths as a function of time of exposure.

The incident radiant exposures required to cause various levels of thermal damage to the 4 fabrics investigated are given in TABLES 5 through 8, for both the simulated-nuclear-weapon and constant-irradiance exposures. The data given represent the best estimates from the experience of 1500 exposures on the

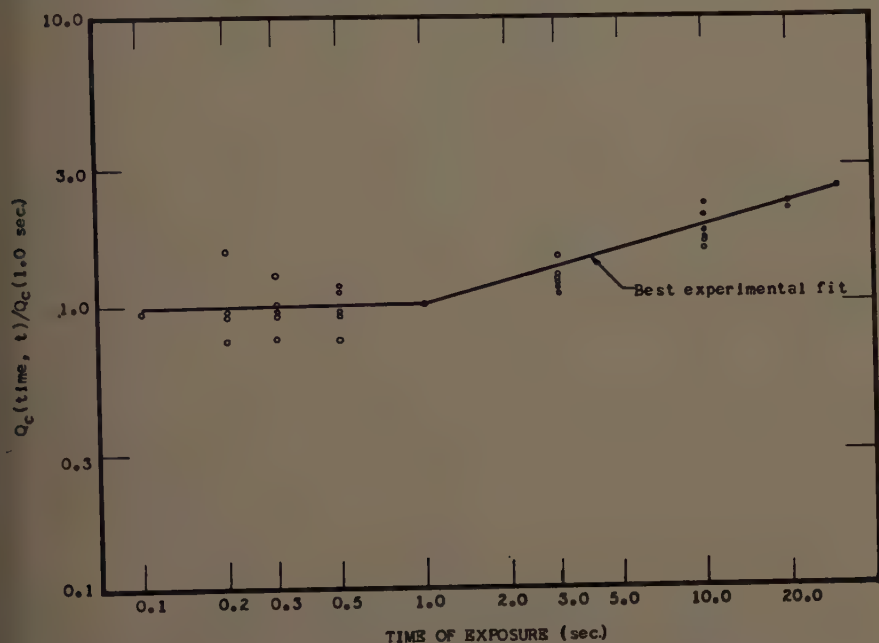


FIGURE 7. Critical radiant exposure corresponding to complete destruction of cloths as a function of time of exposure.

TABLE 4  
DEPENDENCE OF RADIANT EXPOSURE FOR CLOTH DAMAGE ON TIME OF  
EXPOSURE—RECTANGULAR PULSES

Cloth damage	$\log (Q/Q_{1.0})/\log t$	
	$t \leq 1.0$	$t > 1.0$
Threshold damage.....	0.27	0.27
Char-through.....	0.00	0.27
Complete destruction.....	0.00	0.27

4 cloths. The lower limit of exposure times was imposed by the maximum irradiance available at the time of this study.

The correlation between the radiant exposure ( $Q$ ) to cause thermal damage to the 4 cloths and the time of exposure ( $t$ ) is given in TABLE 9, which lists the empirical constants  $a$  and  $b$  in the expression

$$Q = at^b$$

where  $t$  denotes the total exposure time for the constant-irradiance exposures and the time to maximum irradiance in the case of the nuclear weapon pulses.

It is to be noted that the average value of  $b$  for the constant-irradiance exposures, 0.21, is slightly less than that for the nuclear weapon pulses, 0.24.

TABLE 5  
RADIANT EXPOSURES FOR THERMAL RADIATION EFFECTS ON BLUE DENIM

Effect	Constant-irradiance exposures		Nuclear weapon pulses	
	$Q$ (cal./cm. <sup>2</sup> )	$\tau$ (sec.)	$Q$ (cal./cm. <sup>2</sup> )	$t_m$ (sec.)
Threshold scorch	4.6	0.42	7.3	0.33
	6.6	0.91	7.5	0.47
	7.2	2.15	9.7	0.90
			11.7	1.50
Back effect			12.8	2.30
	9.4	0.85	9.3	0.42
	8.5	2.5	8.4	0.53
			9.7	0.90
Destruction by glow			11.7	1.50
			12.8	2.30
	12.3	1.12	11.5	0.52
	17.0	2.35	12.6	0.80
	14.1	4.10	14.3	1.33
			16.0	2.04
			15.9	2.87

TABLE 6  
RADIANT EXPOSURES FOR THERMAL RADIATION EFFECTS  
ON KHAKI COTTON TWILL

Effect	Constant-irradiance exposures		Nuclear weapon pulses	
	$Q$ (cal./cm. <sup>2</sup> )	$\tau$ (sec.)	$Q$ (cal./cm. <sup>2</sup> )	$t_m$ (sec.)
Threshold scorch	7.1	0.65	6.9	0.32
			9.4	0.61
			11.6	1.10
			12.6	1.42
Destruction by glow	13.4	1.23	11.2	2.00
			14.5	0.67
			15.9	1.02
			16.0	1.50
			18.5	2.40
			18.0	3.16

There is a significant difference between the value for the wool gabardine, 0.13, and the average value, 0.22.

EQUATION 2 may be written, for the two pulses studied,

$$Q_s = a_s \tau^b s$$

and

$$Q_p = a_p t_{\max}^b p, \quad (3)$$

where  $Q_s$  and  $Q_p$  represent the critical radiant exposures for the constant-ir-



radiance and nuclear-weapon pulses, respectively,  $\tau$  is the time of exposure for the constant-irradiance exposures, and  $t_{\max}$  is the time to maximum irradiance for the nuclear weapon pulses.

The laboratory pulse was terminated at a time approximately 9 times  $t_{\max}$ ; the laboratory pulse included 75 per cent of the total energy in the equivalent field pulse. The critical radiant exposure for a given field pulse is related to

TABLE 7  
RADIANT EXPOSURES FOR THERMAL RADIATION EFFECTS  
ON GRAY WOOL GABARDINE

Effect	Constant-irradiance exposures		Nuclear weapon pulses	
	$Q$ (cal./cm. <sup>2</sup> )	$\tau$ (sec.)	$Q$ (cal./cm. <sup>2</sup> )	$t_m$ (sec.)
Threshold scorch	10.9	1.00	16.1	0.76
			15.9	1.02
			16.5	1.67
			18.5	2.32
			17.8	2.60
Crinkled	14.4	1.32	21.0	0.99
			22.0	1.41
			22.0	2.13
			27.0	3.47
			25.7	3.75

TABLE 8  
RADIANT EXPOSURES FOR THERMAL RADIATION EFFECTS  
ON BLUE COTTON CHAMBRAY

Effect	Constant irradiance exposures		Nuclear weapon pulses	
	$Q$ (cal./cm. <sup>2</sup> )	$\tau$ (sec.)	$Q$ (cal./cm. <sup>2</sup> )	$t_m$ (sec.)
Threshold scorch	3.1	0.30	4.9	0.21
	4.5	0.63	5.2	0.44
	4.1	1.20	5.4	0.62
			6.4	1.19
Destruction by glow	7.6	0.73	10.3	0.44
	9.4	1.30	10.4	0.66
	10.9	3.20	12.5	1.06
			14.6	1.69
			20.4	3.85

the critical radiant exposure for the corresponding simulated-field laboratory pulse employed in this study by the simple relationship

$$Q_f = 1.33Q_p \quad (4)$$

In the field the time to maximum irradiance of the principal segment of the heat pulse ( $t_{\max}$ , sec.) is related to weapon yield ( $W$ ,  $kT$ ) according to the relationship

$$t_{\max} = 0.032W^{1/2} \quad (5)$$

EQUATIONS 3, 4, and 5 may be combined to give

$$Q_f = cW^d \quad (6)$$

where  $c$  and  $d$  are empirical constants as given in TABLE 10.

TABLE 9  
CONSTANTS CORRELATING CLOTH THERMAL DAMAGE  
WITH TIME OF EXPOSURE

Cloth	Effect	Constant irradiance exposures		Nuclear weapon pulses	
		a	b	a	b
Blue denim	Threshold	6.3	0.29	9.7	0.32
	Back effect			10.0	0.32
	Destruction	12.5	0.25	13	0.25
Cotton twill	Threshold			11	0.37
	Back effect			13	0.25
	Destruction			15.0	0.17
Wool	Threshold			16.4	0.07
	Crinkled			21	0.13
Chambray shirt	Threshold	4.2	0.22	6.0	0.15
	Destruction	8.4	0.23	12.5	0.32

TABLE 10  
THERMAL DAMAGE TO CLOTH FOR NUCLEAR WEAPON PULSES

Cloth	Effect	Equation (6) constants		Radiant exposure		
				Weapon yield (KT)		
		c	d	100	1000	10,000
Blue Denim	Threshold	4.3	0.16	9.0	13.0	19.0
	Back effect	4.4	0.16	9.2	13.5	19.5
	Destruction	7.3	0.125	13.0	17.5	23.0
Cotton Twill	Threshold	4.1	0.19	9.6	15.0	22.5
	Back effect	7.3	0.125	13.0	17.5	23.0
	Destruction	11.0	0.085	16.5	20.0	24.5
Wool	Threshold	17.0	0.035	20.0	22.0	23.5
	Crinkled	18.0	0.065	24.0	28.0	32.5
Chambray Shirt	Threshold	4.8	0.075	6.7	8.0	9.5
	Destruction	5.5	0.16	11.5	16.5	24.0

From the data of TABLES 9 and 10 one may write that

$$Q_f = 2.0Q_s \left[ \frac{t_{\max}^{0.24}}{\tau^{0.21}} \right]$$

or, more simply, without significant loss of accuracy,

$$Q_f = 2.0Q_s \left[ \frac{t_{\max}}{\tau} \right]^{0.23}$$

In other words, for the same degree of thermal damage, it takes twice as much thermal flux in a field exposure as in a rectangular pulse whose duration is equal to the time to maximum irradiance.

### *Application of Heat-Flow Theory*

The behavior of a cloth under stimulation by intense thermal radiation can be analyzed mathematically, provided certain assumptions are made. The cloths are considered as homogeneous solids that are inert; that is, they undergo no significant phase or chemical change, at least until the onset of "threshold" damage. Their thermal behavior must be completely characterized by a set of constant values of thermal conductivity, density, and heat capacity, in addition to the optical constants. Damage is associated with the attainment of a critical temperature by some part of the cloth. Heat losses from the cloth by convection and reradiation are considered to be negligible. Obscuration of the incident radiation by the evolution of volatile products is neglected. The uniformly irradiated area of the cloth must be sufficiently large that, over a sizeable area, one may neglect heat flow in any direction other than that perpendicular to the surface.

The so-called semi-infinite opaque solid is a passive receiver that extends infinitely far in both positive and negative  $y$  and  $z$  directions, and infinitely far in the positive  $x$  direction, as shown in FIGURE 8a (here  $x$ ,  $y$  and  $z$  refer to the usual coordinate axis system, with the  $x$ ,  $y$ , and  $z$  axes mutually perpendicular). For simplicity, the plane surface of the semi-infinite solid is placed in the  $y$ - $z$  plane, or in the plane defined by the equation  $x = 0$ . This solid, initially at a uniform temperature throughout, has thermal conductivity  $k$ , density  $\rho$ , and heat capacity  $c$ , all in appropriate CGS units; these units are constant both in position and in time.

Now let the plane surface of the solid be exposed uniformly to an arbitrary rectangular pulse of radiant energy. A certain fraction of the radiant pulse will be reflected (it is assumed that the reflectance of the surface is constant), while the remainder is absorbed at the surface. The temperature of the solid will then rise, and it is the temperature-time-space history that is to be found. With these assumptions and with suitable boundary conditions, the temperature-time-space history of the irradiated semi-infinite opaque solid during the heating phase of the pulse may be described by

$$\Delta\theta = \frac{2AHt^{1/2}}{\sqrt{\pi k\rho c}} \left[ e^{-x^2/4ht} - \frac{\sqrt{\pi} x}{2\sqrt{ht}} \operatorname{erfc}(x/\sqrt{4ht}) \right]$$

where  $\Delta\theta$  is the temperature rise ( $^{\circ}\text{C.}$ );  $H$  is the irradiance ( $\text{cal./cm.}^2\text{sec.}$ );  $t$  is the time of reference ( $\text{sec.}$ );  $x$  is the distance into the solid ( $\text{cm.}$ );  $k$  is the thermal conductivity ( $\text{cal./cm.}^2\text{sec.}^{\circ}\text{C./cm.}$ );  $\rho$  is the density ( $\text{gm./cm.}^3$ );  $c$  is the specific heat ( $\text{cal./gm.}^{\circ}\text{C.}$ );  $h$  is the thermal diffusivity ( $k/\rho c$ );  $A$  is the radiant absorptance; and

$$\operatorname{erfc}y = 1 - \frac{2}{\sqrt{\pi}} \int_0^y e^{-x^2} dx$$

The expression for the temperature rise of the irradiated surface of a semi-

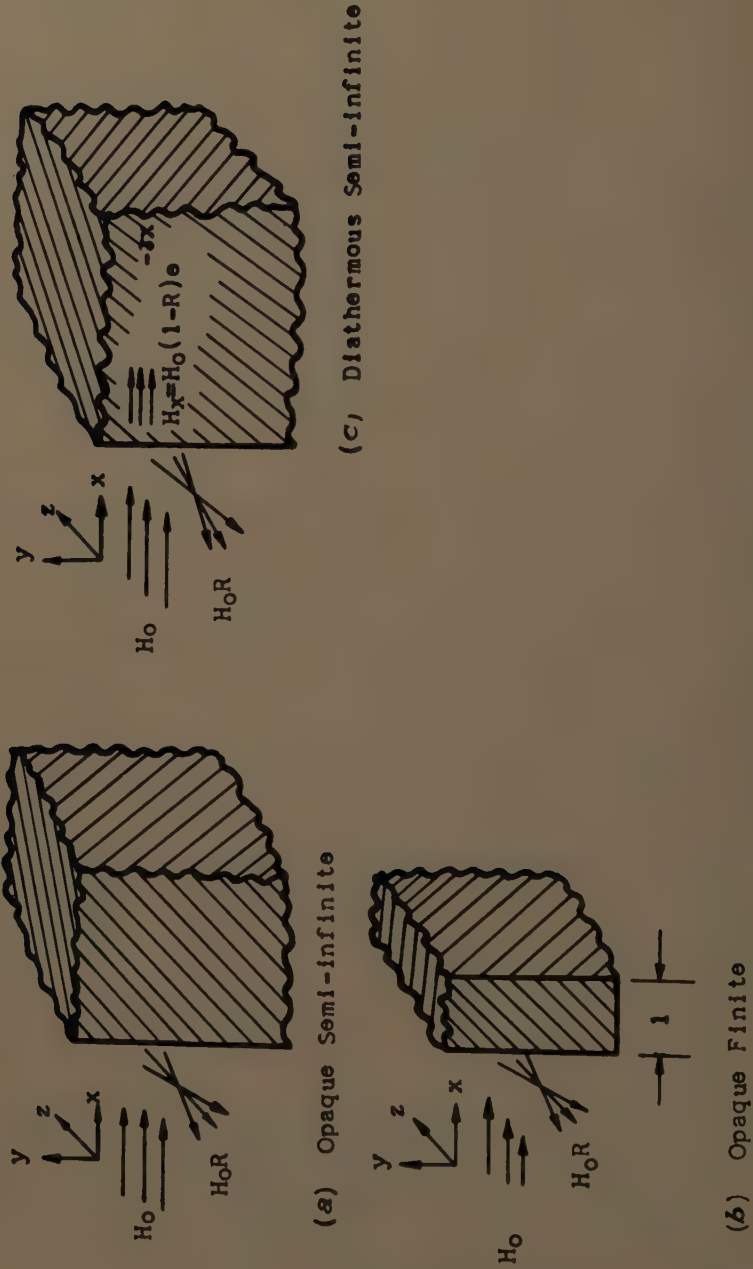


FIGURE 8. Mathematical models of an irradiated cloth.



infinite opaque solid reduces to

$$\Delta\theta = \frac{2AHt^{1/2}}{\sqrt{\pi k\rho c}}$$

or, since the radiant exposure  $Q$  is equal to  $Ht$ , we may finally write

$$Q = \frac{(\Delta\theta)\sqrt{\pi k\rho c}}{2A} t^{1/2} \quad (7)$$

In terms of the maximum temperature rise,  $\Delta\theta_{\max}$ , associated with a pulse of  $\tau$  seconds,

$$Q = \frac{(\Delta\theta_{\max})\sqrt{\pi k\rho c}}{2A} \tau^{1/2}$$

The radiant exposure required to produce a given maximum temperature rise of the surface of an irradiated semi-infinite diathermous medium (FIGURE 8b) is

$$Q = \frac{\Delta\theta_{\max}\sqrt{k\rho c}}{(1-R)} \tau^{1/2} \left[ \frac{e\gamma^2 h\tau}{\gamma\sqrt{h\tau}} \operatorname{erfc}\gamma\sqrt{h\tau} - \frac{1}{\sqrt{h\tau}} + \frac{2}{\sqrt{\pi}} \right]^{-1} \quad (8)$$

where  $h$  is the thermal diffusivity of the medium,  $k/\rho c$ ;  $R$  is the reflectance of the medium;  $\gamma$  is the extinction coefficient ( $\text{cm.}^{-1}$ ), and the other symbols have the same meaning as before.

The radiant exposure associated with a given maximum temperature rise of the irradiated face of an opaque medium of finite thickness,  $\ell$ , (FIGURE 8c) is given by

$$Q = \frac{\Delta\theta_{\max}\sqrt{\pi k\rho c}}{2A} \tau^{1/2} \left[ 1 + 2 \sum_{n=1}^{\infty} e^{-(2nz)^2} - 2\sqrt{\pi}nz \operatorname{erfc}(2nz) \right]$$

where  $z = \ell/2\sqrt{ht}$

The critical energy required to damage a cloth, assuming the cloth to be a semi-infinite opaque solid defined by EQUATION 7 and employing the material constants given in TABLE 1, has been computed for a 1-sec. rectangular pulse. The ratio of the experimentally determined critical radiant exposure to the calculated value, for the three damage levels investigated, is as follows: (1) threshold damage,  $2.44 \pm 0.40$ ; (2) char-through,  $2.96 \pm 0.46$ ; and (3) destruction,  $4.75 \pm 1.68$ .

On the assumption that the cloth is a semi-infinite diathermous medium defined by EQUATION 8 and on the basis of the material constants of TABLE 2, the ratio of the experimentally determined value to the calculated value for a 1-second exposure is given by: (1) threshold damage,  $1.60 \pm 0.76$ ; (2) char-through,  $2.10 \pm 0.38$ ; and (3) destruction,  $2.67 \pm 0.73$ .

The critical radiant exposure has been computed for rectangular pulses for several times of exposure, assuming the semi-infinite opaque solid and semi-infinite-diathermous solid analogues. The data, which are included in FIGURE 5, indicate that the semi-infinite diathermous medium expresses the physical situation satisfactorily for exposure times of 1 sec. and less, but fails to predict the observed radiant exposure for the longer exposure times.

*Conclusions*

It may be concluded that reciprocity holds for constant-irradiance pulses of intense thermal radiation applied to cloths, for char-through and complete destruction, only for exposure times equal to or less than 1 sec. For threshold damage for these times and for all three levels of damage for exposure times greater than 1 sec., the critical radiant exposure is not constant, but is proportional to approximately the one-fourth power of the exposure time. The mathematical analogue of a diathermous semi-infinite solid approximates threshold damage data for exposure times less than 1 sec., provided a constant compensating factor is included in the computations.

*Summary*

The total energy (radiant exposure) required to produce a given level of damage in a material is dependent on the time during which the material is irradiated and the rate at which the energy is applied (irradiance). The purpose of the study was to determine the nature of this relationship for fabrics: (1) for constant-irradiance pulses with total exposure time ranging from 0.1 to 60 sec.; and (2) for exposures in which the irradiance varied with time in a manner similar to that of the thermal radiation emitted during a nuclear detonation.

Several cotton and wool cloths were exposed to the three carbon-arc sources employed in the laboratory studies. The exposures were correlated with the sources for the purpose of extending the usefulness of the data.

The results of the constant-irradiance pulse studies indicate that reciprocity holds, for char-through and for complete destruction, only for exposure times equal to or less than one sec. For threshold damage for these times and for all 3 levels of damage for exposure times greater than one sec., the critical radiant exposure is not constant but is proportional to approximately the one-fourth power of the exposure time. The mathematical analogue of a diathermous semi-infinite solid explains threshold damage data for exposure times less than 1 sec., provided a constant compensating factor is included in the computations.

For pulses simulating the thermal radiation characteristic of a nuclear weapon, the critical radiant exposure is proportional to approximately the one-fourth power of the time to maximum irradiance, or the one-eighth power of the weapon yield.

The relationship between the radiant exposure for an equivalent weapon pulse,  $Q_f$ , with a given time to maximum irradiance,  $t_{\max}$ , and the radiant exposure,  $Q$ , for a constant-irradiance pulse of exposure time,  $\tau$ , was determined to be

$$Q_f = 2.0 Q_s (t_{\max}/\tau)^{0.22}$$

# THERMAL REQUIREMENTS FOR FUNCTIONAL TEXTILES

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We all know that modern aircraft, through the ability to maintain continuous speeds in excess of Mach 1, have placed excessive burdens on those responsible for development of materials capable of withstanding high temperatures. These temperatures, of course, are created by aerodynamic and engine heating. Also, textiles have a place in these aircraft in many unusual applications. To visualize the part textiles play in these new and high-speed combat aircraft, three factors must be realized: (1) crews and equipment must be protected from aerodynamic heat and blasts of high intensity radiant heat; (2) weapons must be delivered with a controlled accuracy; and (3) deceleration of the aircraft, if required in an emergency, and safe recovery of the crew must be ensured.

With respect to the first factor, fibrous battings and coated fabrics are used to impart the necessary protection. In the latter two areas, textiles are used in the form of parachutes to obtain the desired results. Before considering the details of materials used and needed, a look at the areas of concern is in order. FIGURES 1 to 6 will give the reader an idea of them, including thermal blanket, sun shade, the weapons-delivery chute, recovery of aircraft, re-entry, and the latest personnel parachute. These are the general areas that I propose to discuss, including what is used in the way of textile materials, deficiencies that exist, approaches being studied and, ultimately, what is required for an optimum material. To simplify this discussion, I shall classify materials used in two categories: parachute materials and functional materials. Because the latter require minor consideration, I shall discuss them first.

One aeronautical area where thermal radiation constitutes a major problem is insulation for personnel and equipment in aircraft. Normally these blankets consist of: (1) coated fabric; (2) Fiberglas batting; (3) cotton or nylon scrim (optional); and (4) vapor barrier. To prevent water penetration, sewn quilting has been eliminated in favor of new high-temperature adhesives. In this application light weight, excellent tear strength, and flame resistance are required for the coated fabrics. A coated fabric that will take the vertical flame test described in CCC-T-191b, with a maximum of 2 seconds' flame time and 3 seconds' glow time, is considered satisfactory. Of course, it must be remembered that the fabric cannot promote corrosion (that is, coating). Let me add another and somewhat new requirement. I know that Mylar and Polyethylene, which are vapor barriers, fail at low temperature. Most of the coatings cannot withstand much more than 450° F. We are now interested in temperatures of 700° F. built up by aerodynamic friction on the aircraft skin. Even higher temperatures can exist; for actual data we must wait until some of the newer aircraft are flight-tested. It is obvious that it will be necessary to replace some of the present vapor-barrier materials. Coatings will be called on to withstand temperatures of 700° F. for periods of 10 to 30 sec. The basic fabric must be just as resistant to heat as the coating. On this application the weight will be very important. Weights of less than 3 oz./sq. yd. for the coated

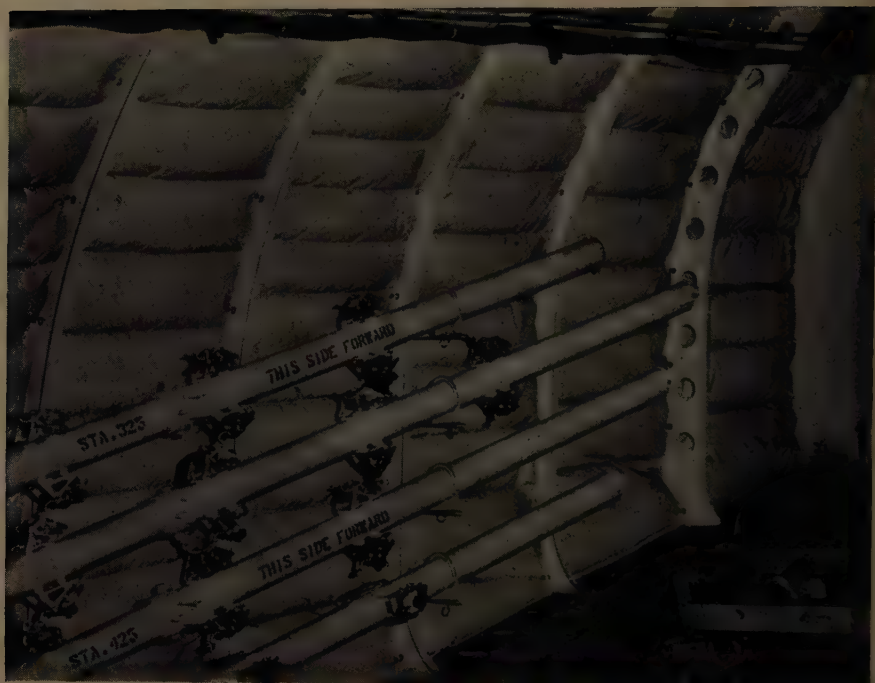


FIGURE 1.

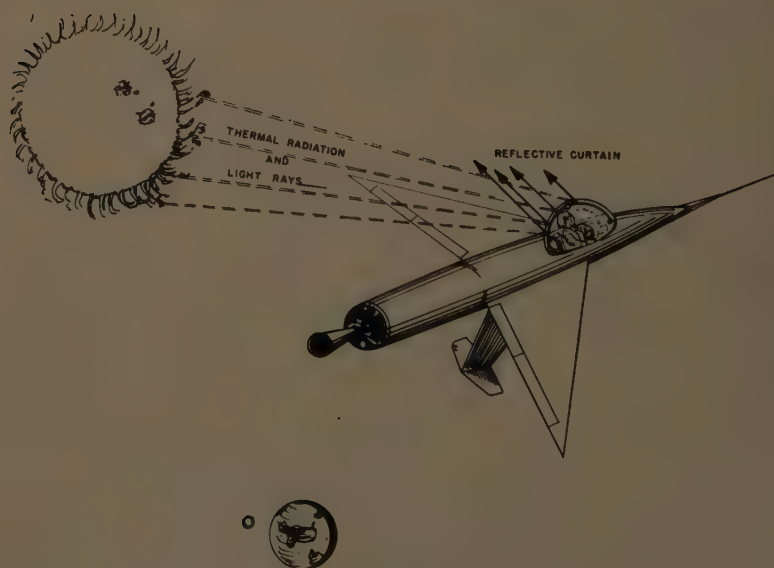


FIGURE 2.





FIGURE 3.

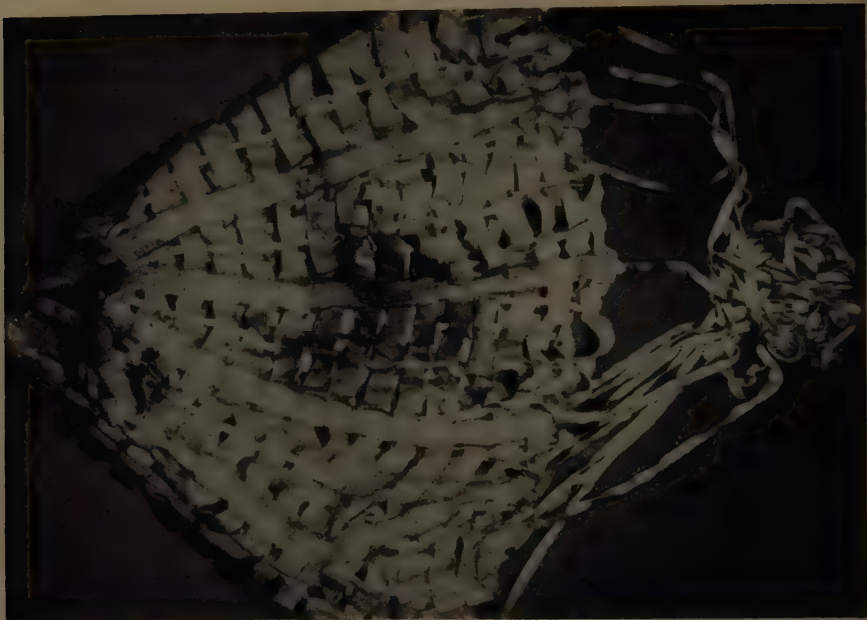


FIGURE 4.



FIGURE 5.

fabric will be a very important requirement. Strength will not be of concern since this material will lie against the aircraft skin.

Protection of the crew of an aircraft from thermal radiation can be a great problem. Because of man's limited ability to take blasts of very high-intensity






FIGURE 6.




radiant heat and the accompanying light, protection must be sufficient to prevent the impairment of efficiency. Much has been done in the evaluation of textile materials for crew hood curtains. In the establishment of data on the thermal capacity of textile materials, Department of Defense agencies and at least two aircraft companies using such materials have been dominant. Although the specific requirement cannot be given for reasons of security, most

material evaluation procedures and data are publishable. A primary means of evaluating potential thermal curtain or crew hood materials has been the utilization of carbon arcs. Two procedures have been thoroughly evaluated. The first uses two searchlights: one to throw the light (and heat) to an equal, at a given distance, where the mirror refocuses on the sample. The second utilizes a motion-picture type of projector that focuses the heat and light on a given area. Another and more recent procedure involves the use of banks of radiant-heat lamps with mirrors behind and on all four sides to direct the heat toward the sample. Although it may not be the wisest comparison, I propose to show what occurs when data on similar fabrics obtained on three different concepts of thermal sources are compared (TABLE 1). During the last three

TABLE 1  
COMPARISON OF THERMAL SOURCES

Sample	Radiant heat lamps		
	Flux	Total input	Percentages transmission
 Silicone rubber coated glass	15 Cal./cm. <sup>2</sup> —sec.	41.5 Cal./cm. <sup>2</sup>	17
 Aluminized vinyl coated cotton	15 Cal./cm. <sup>2</sup> —sec.	25.0 Cal./cm. <sup>2</sup>	0
 Bleached cotton duck *	15 Cal./cm. <sup>2</sup> —sec.	42.0 Cal./cm. <sup>2</sup>	12

Projector arc source			Twin search light		
Flux	Total input	Percentage trans.	Flux	Total input	Percentage trans.
 25 Cal./cm. <sup>2</sup> —sec.	25 Cal./cm. <sup>2</sup>	2.8	20 Cal./cm. <sup>2</sup> —sec.	75 Cal./cm. <sup>2</sup>	6.9
 —	—	—	20 Cal./cm. <sup>2</sup> —sec.	41 Cal./cm. <sup>2</sup>	0
 19.7 Cal./cm. <sup>2</sup> —sec.	37.0 Cal./cm. <sup>2</sup>	0	20 Cal./cm. <sup>2</sup> —sec.	48 Cal./cm. <sup>2</sup>	—

\* Two layers

years we have made constantly increasing efforts to obtain better materials because of continuous changes made in requirements. The latest requirement has established, in effect, a maximum tolerable light transmission (of 0.015 per cent) based on present thermal flux requirements. To compound the problem, a 50 per cent lighter fabric is desired. Since light transmission can be reduced by increasing thickness or density and since heat can be best reflected by white surfaces, it becomes obvious that any material will not be suitable. An ideal fabric could possibly be one of glass yarn coated with white silicone, Viton, or Hypalon, and having an overcoating of finely divided aluminum.

Another area in which the same type of thermal radiation has created problems is weapon delivery. To control speed and accuracy of delivery, parachutes can be used to ensure weapon delivery. Preliminary tests conducted at the Pacific Proving Ground indicated that thermal radiation could cause failure



in parachutes at a considerable distance from a detonation. FIGURE 7 shows one of the first indications of this effect, namely, burning of the dark ink numbers. Because of this type of damage a series of tests was conducted: one to determine the effect of ink on parachute ribbon strength, and another to determine the effect of sewing thread color on seam strength.<sup>4</sup> TABLE 2 presents these data. Additional studies<sup>5</sup> showed, as presented in TABLE 3, that the color of webbing and flux can affect the resistance of the materials. In this area even dirt spots or dirty yarns can destroy as much as 25 per cent of the strength. Because the thermal effect is so critical, cleanliness of materials and even the

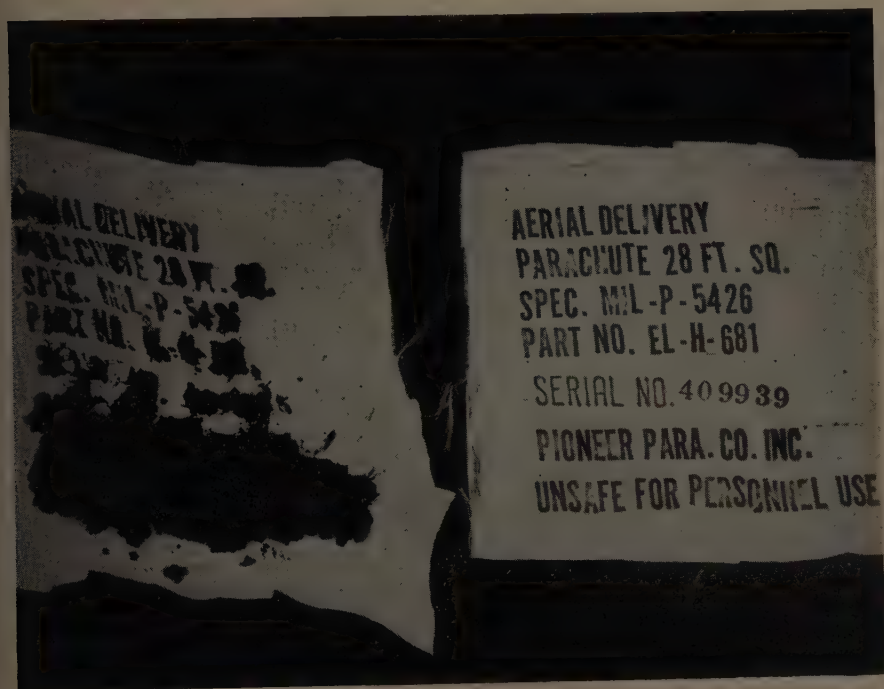




FIGURE 7.

elimination of colored marker threads is required. To make thoroughly sure of the capability of these ribbons to resist damage, their strength was determined by exposing them to thermal testing and by prestressing samples in a simulated air flow past them. Their ambient temperature at altitude is also being determined. The parachutes are stored under extreme environmental conditions and, in addition, they now, under proposed requirements, must retain all strength after 5 hours' exposure to 250° F. This will severely tax presently specified Type-300 or HBT Nylon 66. I question the feasibility of using such yarns in future parachutes of this type. Possibly Type 330 or the equal of Nylon 66 or a modified form of Nylon 6 could be used. One step further could be the use of a yet-to-be-produced high-temperature nonmelting organic fiber. Much exploration will be necessary in this area.

TABLE 2  
RIBBON STRENGTH

Inked samples					
Width of marking		Total exposure		Breaking strength, lb.	
	1/2 inch	Control		910	
		25 Cal./cm. <sup>2</sup>		270	
		10 Cal./cm. <sup>2</sup>		350	
	3/16 inch	Control		890	
		25 Cal./cm. <sup>2</sup>		280	
		10 Cal./cm. <sup>2</sup>		295	
	1/8 inch	Control		948	
		25 Cal./cm. <sup>2</sup>		250	
		10 Cal./cm. <sup>2</sup>		350	



Seam samples					
OD sewing thread			Natural sewing thread		
Flux	Total exposure	Breaking strength, lb.	Flux	Total exposure	Breaking strength, lb.
	5 Cal./cm. <sup>2</sup> - sec.	25 Cal./cm. <sup>2</sup>	5 Cal./cm. <sup>2</sup> - sec.	25 Cal./cm. <sup>2</sup>	172
		15		15	218
		5		5	210
		Control		Control	200
	15 Cal./cm. <sup>2</sup> - sec.	25 Cal./cm. <sup>2</sup>	15 Cal./cm. <sup>2</sup> - sec.	25 Cal./cm. <sup>2</sup>	152
		15		15	158
		5		5	198
		Control		Control	200

TABLE 3  
STRENGTH RETENTION

Nylon webbing				Dacron webbing	
Natural		OD		Natural	
Flux and total exposure	Percentages of strength retained	Flux and total exposure	Percentages of strength retained	Flux and total exposure	Percentages of strength retained
25 Cal./cm. <sup>2</sup> - sec.	100.1	85 Cal./cm. <sup>2</sup>		85 Cal./cm. <sup>2</sup>	
		- sec.		- sec.	
		6.7 Cal./cm. <sup>2</sup>	74.5	16.0 Cal./cm. <sup>2</sup>	79.5
		10.0	52.1	24.0	63.8
		13.4	47.0	32.0	14.6
25 Cal./cm. <sup>2</sup>	100.1	20 Cal./cm. <sup>2</sup>		20 Cal./cm. <sup>2</sup>	
		- sec.		- sec.	
		12.0 Cal./cm. <sup>2</sup>	63.3	24.0 Cal./cm. <sup>2</sup>	97.2
		18.0	45.7	36.0	88.2
		24.0	45.6	48.0	45.5

Because heating due to the passage of a device or parachute through upper atmosphere can affect the strength of materials, two distinctly different areas of research are being studied. The first is concerned with parachute ribbons and theoretical calculations of heat build-up at varying altitudes and Mach numbers.<sup>3</sup> Initially, more concern was placed on high Mach numbers and low altitudes (up to 100,000 ft.). FIGURE 8 gives an example of the data obtained. In addition, it was also determined that, based on calculations, the addition of a water-absorbing layer (such as silicone sponge) to each side of the ribbon will provide, when saturated, sufficient coolant to protect the ribbons at speeds of

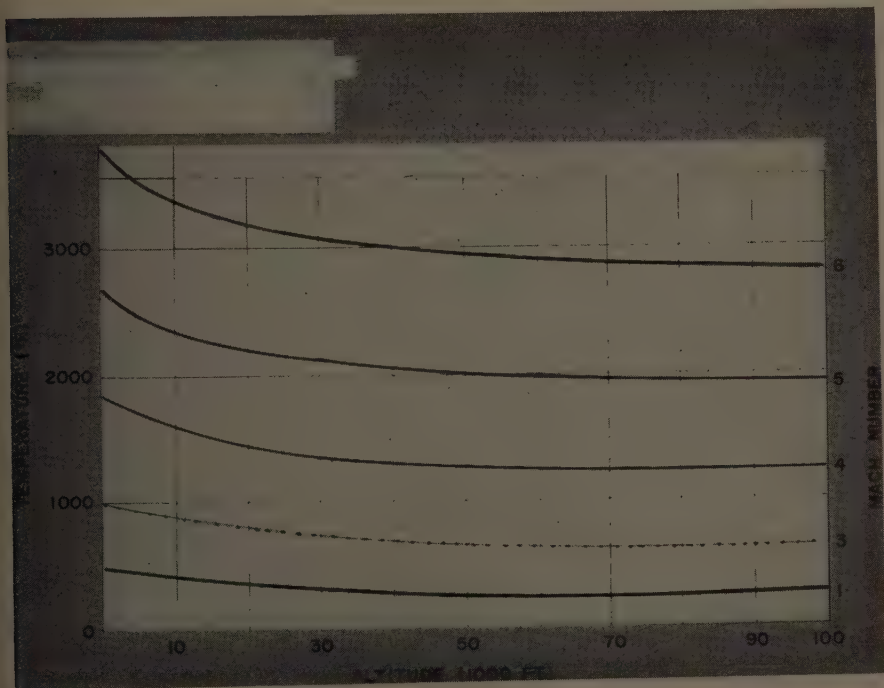


FIGURE 8. Leading edge stagnation temperatures.

Mach 5 and at 100,000 feet. Using water, 0.1 lb. of  $H_2O$ /ft.<sup>2</sup> would be required. If a sublimating coating such as hexachloroethane is used, 1 lb./ft.<sup>2</sup> would give the same protection to the ribbon. To explore this area further, a series of tests was conducted at Arnold Engineering Development Center, Tullahoma, Tenn. Using a wind tunnel, the following conditions were obtained: (1) Mach 5 airflow; (2) density equivalent to 100,000 feet; and (3) air preheated to 900° F.

From these studies it becomes apparent that the addition of certain chemical compounds can give nylon an added life in uses where forward velocities can create an oblatting effect.

It has already been realized that present fibers cannot meet all of the requirements that are now being formulated for use in re-entry type decelerations. Now that we have considered the environments to be experienced during flight

in space and deceleration (in space or on entering an atmosphere), it appears that a new concept of textile fibers will be required. To this end we have initiated a series of programs aimed at the ultimate development of metallic- and ceramic-type continuous-filament yarns capable of being woven into textile type materials. Two of these programs are concerned primarily with the actual feasibility of producing such fibers. A program now being initiated deals with molybdenum fibers (down to one-half mil diameter), which have an excellent resistance to heat but are seriously affected by oxidation and corrosion. To alleviate this, our program will evolve techniques of applying nickel and chromium coatings to the fibers. Subsequent tensile tests at temperatures, coupled with tests to determine corrosion and oxidation effects, will be undertaken. This is one approach to a complex fiber problem. Still to be considered

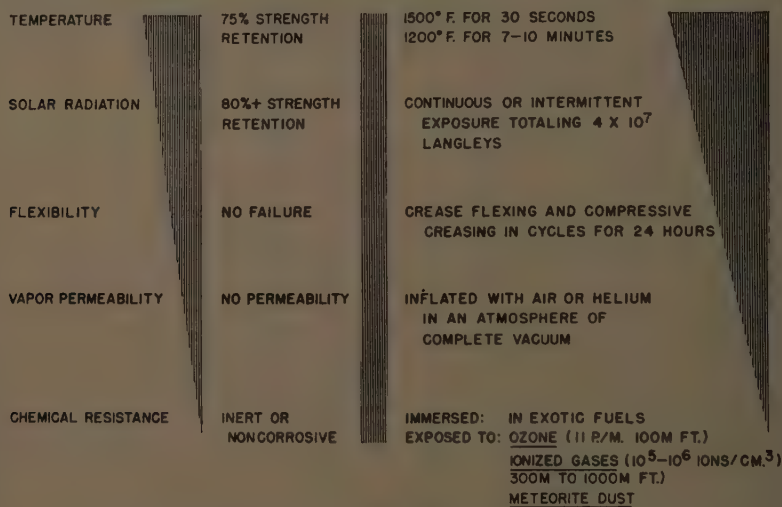


FIGURE 9. Target requirements.

is the radiation that exists in the upper atmosphere. In this respect, ozone, ionized gases, and very concentrated ultraviolet light effects must be determined. Target requirements in this particular area are shown in FIGURE 9.

One other area of thermal damage bears sufficient importance to warrant discussion here and investigation by the Air Force. The background or cause for initiation of our present studies came from a series of field reports indicating that personnel parachute packs and harnesses were being sufficiently damaged during in-flight aircraft fires to cause parachute malfunctions. A few of these are as follows: (1) riser on personnel parachute in B-47 was burned during fire in flight; (2) entire pack fused closed in attempt to leave fire-filled B-52, the chute failing to function; (3) one riser of four burned through and failed on opening, the other three operating safely; and (4) aircraft crashed and burned, and parachute was destroyed, indicating that in-flight ejection would have resulted in failure.

One of these parachutes is shown in FIGURE 10. Initially, a program aimed



at the development of heat-reflecting materials to cover in-use nylon materials was conducted. Field tests using JP-4 (jet) fuel as a heat source gave a fair reproduction of the aircraft fire conditions reported. The materials evaluated were primarily asbestos with an aluminum surface. Results of these so-called fire tests showed that protection could be achieved. FIGURE 11 shows a fire-seared pack. FIGURE 12 shows the same pack after the ripcord was pulled.

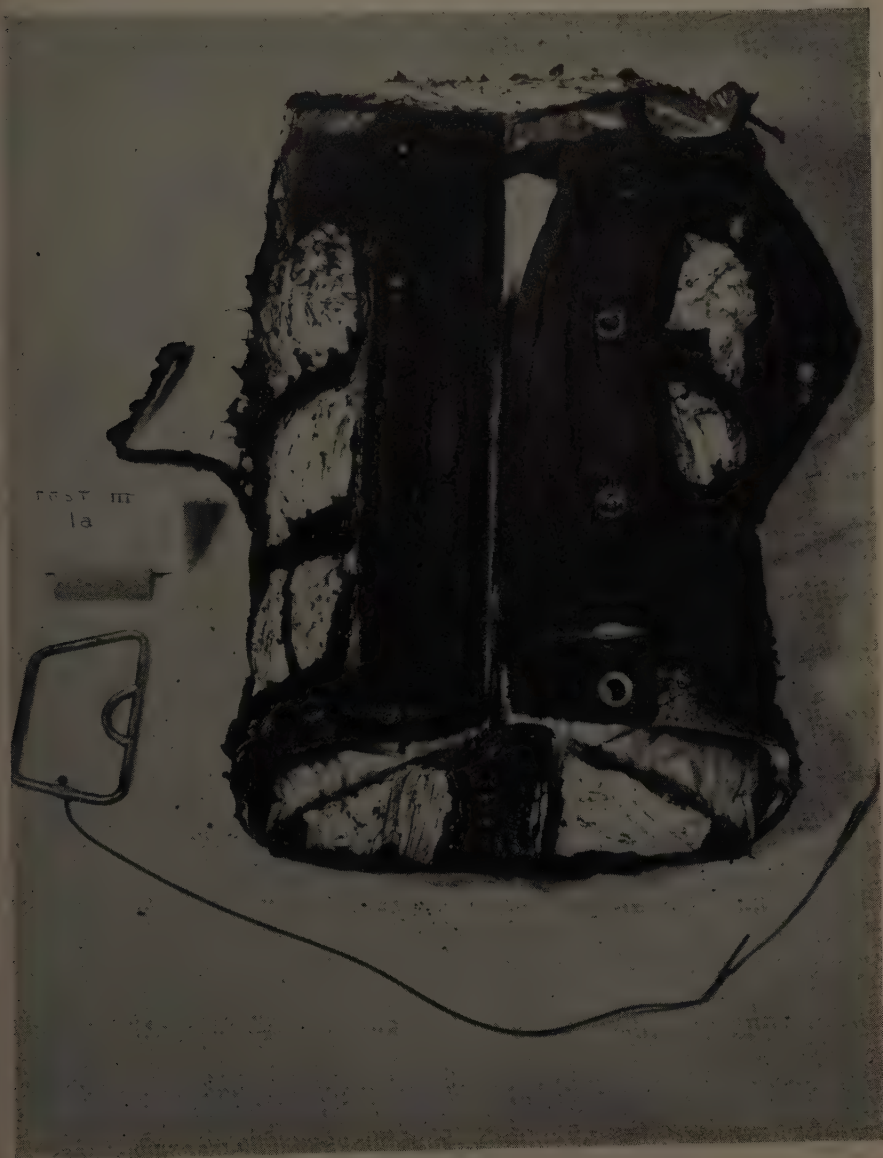


FIGURE 10.

However, a prime requirement for aircraft equipment would be violated if this type of material were utilized: this factor, of course, is weight. Another compounding factor is that actual wear tests of parachute packs using aluminum-coated fabric show that the service life of the material would be drastically reduced. Consequently, a new concept of protection from heat and the flames

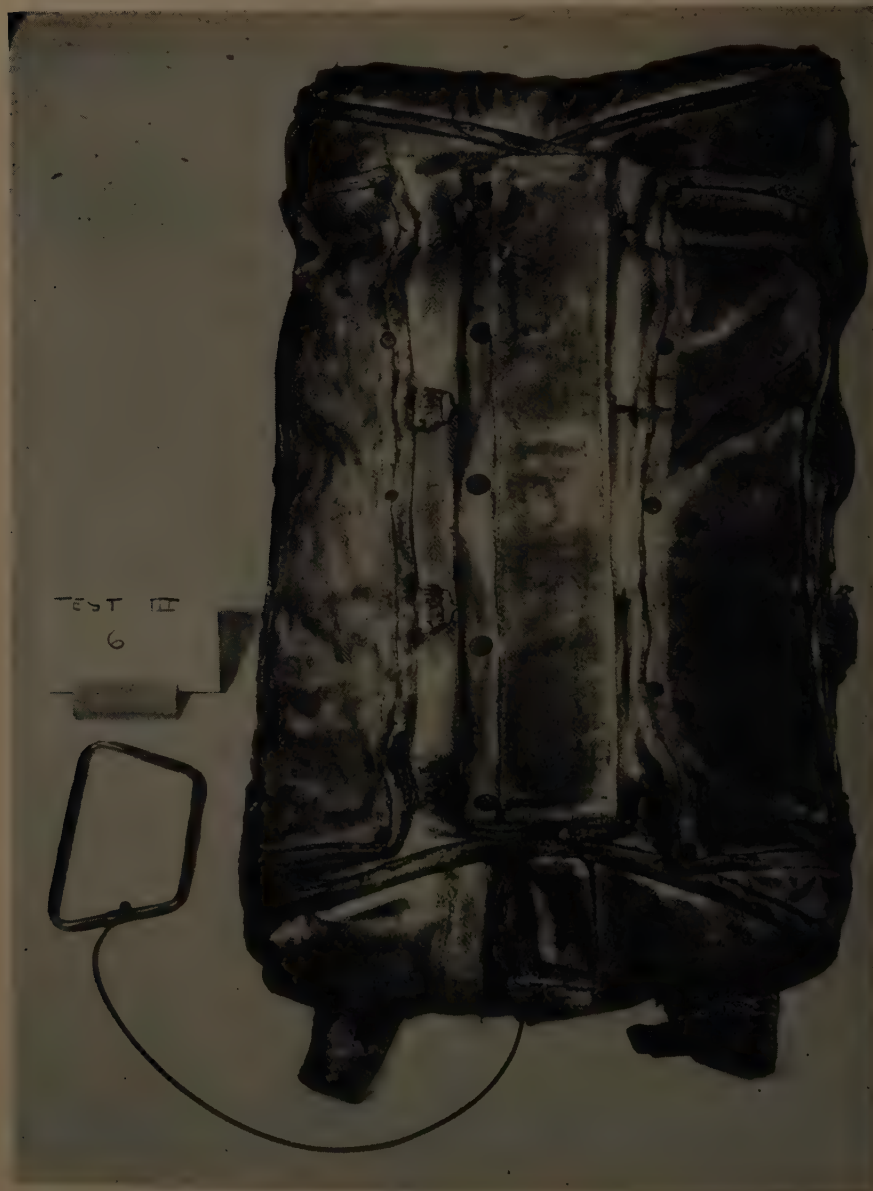


FIGURE 11.

of aircraft fires must be developed in order to fulfill such requirements as: (1) withstanding direct immersion or exposure to fire or heat of  $1200^{\circ}$  F. for 12 sec. (2) keeping the weight and bulk of materials in the range of the present 7-oz.

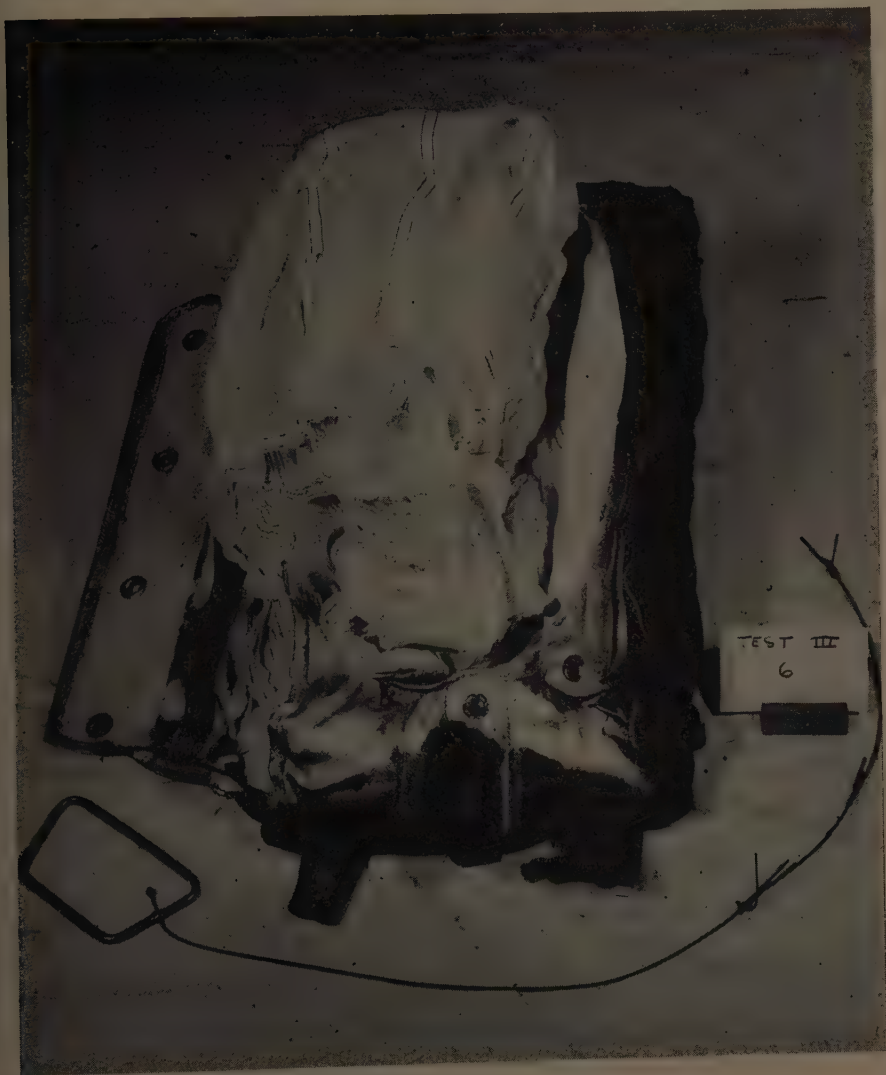


FIGURE 12.

fabric and 6000-lb. webbing; (3) maintaining flexibility for pack integrity and fitting and harness comfort without compromising adjustability; and (4) making no change that would affect the service life of any material.

A concept that is not considered new is the use of a nonmelting fiber for fabric and webbing; however, this would require a new nonmelting fiber to meet all

of our requirements. An approach that I feel is very possible is the utilization of intumescent coatings. The swelling or expanding of these coatings on the surface of a fabric could very well create an insulation that would give the desired protection for a period of 10 to 12 sec.

This is not the first time that I have discussed Air Force textile requirements publicly.<sup>2</sup> However, it is seldom that we have the opportunity to expound the facts about thermal damage, its effect upon textiles, and means of protecting them from it, as well as those requirements in which the textile industry and textile research organizations could be interested. Success in furnishing temperature-resistant textiles for use in functional Air Force uses can be achieved only through a continuing cooperative effort with industry.

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## TEXTILE RESEARCH: A CHALLENGE

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Until recently the development of functional textiles was concerned primarily with such factors as cost, availability, aesthetics, strength, and protection against the natural elements, wind, rain, and snow. This picture was not essentially changed by the advent of new man-made fibers and functional finishes. As long as a fiber or finish was not too expensive and provided some improvement in one or more of the normal values of strength, wear resistance, crease retention, wrinkle recovery, and other such factors, its consideration was fully justified.

The scientific revolution of the last few years, however, now promises to alter greatly the world in which we live. A new era of unbelievable power, of ultrasonic speed, and of exotic fuels and chemicals has been opened to us. The ability to utilize, control, and withstand these new tools requires the more efficient utilization of materials, especially textiles. In addition to looking and feeling like a good piece of cloth, fabric now may be required to satisfy such diverse end-use requirements as keeping a man's blood from boiling in a rarefied atmosphere or protecting him against atomic heat and radiation, jet exhaust, high temperature, extremely corrosive missile fuels, toxic chemicals, and many other dangers. While these factors, initially, are of principal importance in military operations, industry support, and the long-range delivery potential of missiles, submarines and aircraft make them of considerable importance in civil defense, transportation, and industry. If the full potential of these developments is to be realized, we must rapidly learn more about how to live, work, and fight in the atomic-space age.

To accomplish this objective we must first review and establish requirements, determine how best to utilize the materials now available, and conduct integrated studies leading to the development of improved materials and methods of application. Fortunately, we have a rapidly expanding range of tools to work with, including a variety of new fibers, finishes, processing techniques, and engineering know-how. Unfortunately, however, many of these new tools bring with them additional problems of their own. An example is the thermoplasticity and melt-and-flammability behavior of high-strength synthetics such as nylon and polyester fibers. Thermoplasticity is a limiting factor in high-speed drag parachutes and webbing, and melt-and-flammability characteristics can pose serious problems in clothing and tentage. A fiber that melts may cause serious melt burns or cause a fabric to lose prematurely its protective cover value in clothing. At the same time the use of blends of fibers or finishes that eliminate melt drip of molten polymer may actually increase flammability.

Since the melting and thermal disintegration of textiles is now recognized as a major concern in protecting man and developing space-age equipment, it is becoming an important area for expanded research. While some improvements may result from further studies of fabric geometry, color, and clothing engineering, most promise appears to lie in the fields of new fiber research, fiber blending, new finishes and coatings, and fiber modification. A new low-cost

organic or organometallic fiber combining high-temperature stability with good general-purpose textile qualities would help meet many current requirements. Meanwhile, considerable effort is being made to improve further the utility of existing fibers. The Navy Clothing and Textile Research Laboratory of the Bureau of Supplies and Accounts, for example, is supporting a three-phase orientation program aimed at upgrading the melt resistance and thermal stability characteristics of the newer high-strength man-made fibers. The use of blends of thermoplastic synthetic fibers with rayon, cotton, and other fibers is being explored at the Navy Clothing and Textile Research Laboratory and at the Textile Research Institute. The interaction of fibers and coatings is being investigated at the Textile Research Institute and, finally, methods of chemically modifying fibers are being studied at the Institute of Polymer Research at the Polytechnic Institute of Brooklyn.

Another consideration that is greatly complicating material and clothing research, particularly in the military, is a very practical one. Military concepts are being revolutionized with emphasis on firing power and range, speed, and mobility. For the fighting man to catch up with this dizzying pace, his greatly increased functional needs must be satisfied with a minimum clothing load and greatly reduced reliance on replacements from reserve stocks. Nuclear-powered ships, for example, may operate afloat for greatly extended periods and over vast areas. At the same time, the long-range surprise-attack potential with an increased variety of much more powerful weapons has greatly increased. Thus constant preparedness becomes a more pressing problem.

While it may be relatively easy to design the best possible textile and garment for any one highly specialized need, such a limited-use item will possibly be of little value in highly mobile operations where the fighting man must be prepared for extended protection against two, three, or half a dozen types of offensive weapons successively or simultaneously. The combatant can not have the luxury of a variety of specialized garments in his limited wardrobe or the time to change from one to another. A very real challenge is the need to build as many multifunctional characteristics as possible into both everyday utility clothing and the minimum number of special protective garments.

Each of the armed services attacks this problem from the viewpoint of its specialized needs. The Navy, for instance, emphasizes such factors as waterproofness and flotation. While development is continuing to determine the best possible solution to each of today's and tomorrow's specialized needs, every effort is made to apply the benefits of these studies to the development of normal utility clothing with greatly increased multifunctional capabilities. A good example of this process can be found in present efforts at the Navy Clothing and Textile Research Laboratory to develop improved general-purpose wet- or foul-weather clothing. The presently used laminated cotton-synthetic rubber-cotton material has low durability and tear resistance, and has a cotton-fabric outer surface that is an excellent dust and spray collector. In addition, the fabric burns easily. Among the new dusts and sprays that may now be encountered at sea are those of atomic fall-out and contaminated water splash from bombings or wash-down operations. Experimental wet-weather clothing is now being made with a high-tear-strength double-coated synthetic fiber fabric having good melt-and-flame resistance and a smooth waterproof outer surface.



FIGURE 1. Experimental Navy wet-weather clothing suitable for possible use in wash-down decontamination operations aboard ship. Photo by Polytechnic Institute of Brooklyn, Brooklyn, N. Y., reproduced by permission of the United States Navy Clothing and Textile Research Laboratory, Brooklyn, N. Y.

This garment is also designed to be used with a gas mask and can probably function aboard ship as a good general purpose decontamination suit for use in hose and spray wash-down operations (FIGURE 1).

In summary, it is apparent that we are entering a new scientific era of greatly extended human capabilities. To realize fully potential benefits and to improve our chances for survival, textiles and clothing far superior to those presently available are required. We must have new fibers, blends, and textiles with increased thermal and chemical stability. We must have textiles and clothing engineered to give maximum efficiency with available fibers and finishes. Accomplishing this textile revolution in time to meet these urgent needs will require intensified efforts to establish necessary background and technical requirements and the close cooperation of industry, educational institutions, and government.



# THERMAL RADIATION BURNS BENEATH FABRIC SYSTEMS

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Almost immediately after the detailed casualty reports from Hiroshima and Nagasaki reached the United States, a number of teams of investigators set out to study the damaging effects of high-energy thermal exposure on skin. Both university and military groups in Brooklyn and Rochester, N. Y., New York, N. Y., Philadelphia, Pa., Virginia, Ohio, and California concerned themselves with various aspects of the problem, and I shall draw upon the contributions of all of these without attempting to give specific credit in each instance.

Within five years, appropriate energy sources had been developed and calibrated, and the various skin parameters involved were defined. Henriques and Moritz, working in Boston, Mass.,<sup>1</sup> by 1947 had shown the vital importance of the thermodynamic constants of skin in burns: namely the thermal conductivity,  $K$ ; the density,  $\rho$ ; and the specific heat capacity,  $C$ . The reflectance of skin was quickly seen to be of critical importance, since energy bouncing off the skin can cause no damage. The thickness and water content of the various layers of the skin of humans and various animals were studied; in general, the skin of young Chester White pigs was found most closely to resemble that of humans.

In the human, three "degrees" of burn are commonly recognized grossly. The Rochester group carefully defined five grades of increasing severity of skin burn<sup>2</sup> as seen in pigs, corresponding roughly to human burns as shown in TABLE 1.

All these grades of burn have been extensively studied microscopically, even to the degree of developing new techniques for staining the tissue to detect "irreversible" damage, as Hinshaw has recently reported.<sup>3</sup>

Visible damage occurs primarily to: (1) surface epithelium; (2) downfolded epithelium of hair roots and glands; (3) fibroblastic cells; (4) collagen; and (5) blood vessels.

Furthermore, the development of a burn is a dynamic process that proceeds rapidly for the first twelve hours postburn, and slowly thereafter, when it overlaps with the processes of healing. It is not necessary to go into detail, but it does seem advisable to emphasize the fact that a burn is an extremely complex phenomenon, and that "degree" is essentially an empirical definition whose accuracy depends upon the precision of the definition.

The nature of thermal transfer within semiopaque, semi-infinite solids under the impact of radiant energy is an affair of such complexity that the mathematics involved tax the capabilities of most medical men, including myself. Indeed, without accurate knowledge of the physical constants of skin (some of which are currently not very precisely known), the time-temperature-depth history of skin in response to a given dose of radiant energy cannot be computed with any degree of confidence. Furthermore, the accurate measurement of rapid temperature changes in the outer laminae of skin at shallow depths has proved thus far to be an insuperable problem, although the attack currently

being made upon the problem by T. P. Davis at Rochester, N. Y., appears to hold considerable promise.

From the above, it is obvious that at the present time we do not know very precisely the conditions of time and temperature necessary to produce irreversible damage to the biological system known as the skin. This has not, however, prevented us from developing theories to account for such facts as we do observe. The earliest such theorem to fit the facts was developed by F. C. Henriques in 1947, and has been extensively cited since that time. James D. Hardy, now of Philadelphia, Pa., has independently pursued this problem by very ingenious methods, showing the relationship of pain to irreversible damage and the critical change occurring at 45° C.,<sup>4</sup> below which reparative or anabolic processes overbalance the catabolic or destructive reactions. Above this point, the catabolic rate exceeds the anabolic, and irreversible damage eventually occurs. Charles H. Fugitt has presented a rate-process theory of thermal injury based upon the van't Hoff reaction isochore and the Arrhenius equation.<sup>5</sup> He showed that the data available in 1955, when treated in this manner, fitted theory best if it were assumed that at least two simultaneous degradative proc-

TABLE 1

Pig		Human	
Grade	Criterion	Degree	Criterion
1	Persistent redness	1	Persistent redness
2	Patchy whiteness	2	Blister formation
3	Solid white	2	(Full thickness)
4	Steam bleb		
		3	Charring
5	Carbonization		

esses were in operation at different reaction rates. Basically, this amounted to an extension and clarification of Henriques' damage-integral treatment. It appears probable that the latter attack will have even wider application as more physical information becomes available. It further seems quite probable that Hardy's data and conclusions are perfectly in harmony with Fugitt's analytic method, although I am not aware that any attempt has been made to investigate this.\*

The conclusions above are, of course, based upon accurate knowledge of the rate and amount of energy reaching the skin. From a practical standpoint, it is next to impossible to determine this when fabric is interposed between skin and source, although progress is being made at the present time along two lines. The first is a mathematical treatment of the problems of heat transfer in such systems, which has been worked out in remarkable detail in H. C. Hottel's laboratory. This has not yet been extended to include the case where fabric undergoes either phase or chemical change and, as such, is of distinctly limited applicability in short, high-intensity exposure. The second is the long-con-

\* In a personal communication I was apprised by Alice Stoll, of Hardy's laboratory, that such a computation has been carried out, and shows a parallelism to, if not absolute correspondence with, the data of Hardy's experiments.

tinued effort of the Naval Material Laboratory to develop a skin simulant with physical properties so closely resembling those of skin that time-temperature histories obtained in it may safely be extrapolated to the prediction of burns in animals. Within limits, this goal appears currently to have been attained, although we continue to confirm such predictions by animal exposures, particularly when dealing with previously unfamiliar protective systems.<sup>6a-d</sup>

Nevertheless, despite such progress in the development of theory and analogue, the vast bulk of information upon which we base our present knowledge of subfabric burns is founded upon experiments in which some animal, rat, pig, or human, has acted as the receiver and indicator. Let us now look at the methods by which such data have been obtained.

With the exception of some wide-area studies at Rochester, based upon the use of exploding magnesium powder, and certain very limited studies carried out at field tests of nuclear devices, the available data have been obtained by the use of high-intensity carbon-arc systems such as Thomas Monahan describes elsewhere in this monograph. Details of shuttering, control, pulse shaping, and incident optics differ from laboratory to laboratory; FIGURE 1 shows the system I used at Rochester under Herman Pearse's guidance.<sup>7</sup> Most of what I shall hereafter say will be drawn from that experience, gained in the years from 1952 to 1955, supplemented by subsequent information from that and other laboratories. My exposure port, thermostatically controlled at 36° C., had an aperture 1.7 cm. in diameter; either "square" waves or "shaped" waves of energy could be employed. The young Chester White pig was our receiver and indicator; and our region of maximum interest, insofar as burn was concerned, was the 2-plus level, since this appears to relate closely to the second-degree burn in humans. Prolonged anesthesia was employed, and the burns were assessed after 24 hours as a standard.

It must be understood that variations not only in the arc intensity about its calibrated value, but also in the pig's skin (from pig to pig and from area to area in the same pig) made it necessary for us to employ statistical methods. (The rapid, efficient method of T. W. Anderson, J. M. Tukey and P. J. McCarthy—the so-called "up-and-down" method—was not practicable because of the 24-hour delay between exposure and assessment.) In addition, we felt it advisable to make every effort to avoid both personal bias and systematic error: consequently, the following exposure plan and statistical treatment were worked out.

In a typical experiment, there would commonly be about 18 different combinations of fabric, exposure time, and irradiance comprising the region of interest. Each side of a pig was divided into 36 exposure areas, giving 4 replications of each treatment per pig. The treatments were randomized over the available areas and the exposures delivered according to the random scheme. The following day, each area was assessed for degree of burn, without knowledge of the treatment it had received. These results were then keyed back to the treatment and the results tabulated in the fashion set forth in FIGURE 2.

After about 6 to 24 (usually about 15) replications had been obtained, the data were analyzed by the rapid probit method of Litchfield and Wilcoxon, dividing the responses into those less than 2 plus versus those 2 plus or more. From this, one obtains the median effective exposure required to produce the

2-plus burn, abbreviated as  $2 + EE_{50}$ . At this exposure time and intensity, one half the burns produced by constant repetition will be less than 2 plus, and half 2 plus or more. The 95 per cent confidence limits about this  $2 + EE_{50}$  estimate are also computed (ordinarily, one is satisfied with a 95 per cent confidence interval of  $\pm 5$  to 10 per cent). Thus, for a half-second exposure of bare skin, the  $2 + EE_{50}$  in the pig is 3.8 cal./cm.<sup>2</sup>; one layer of 9 oz. OG

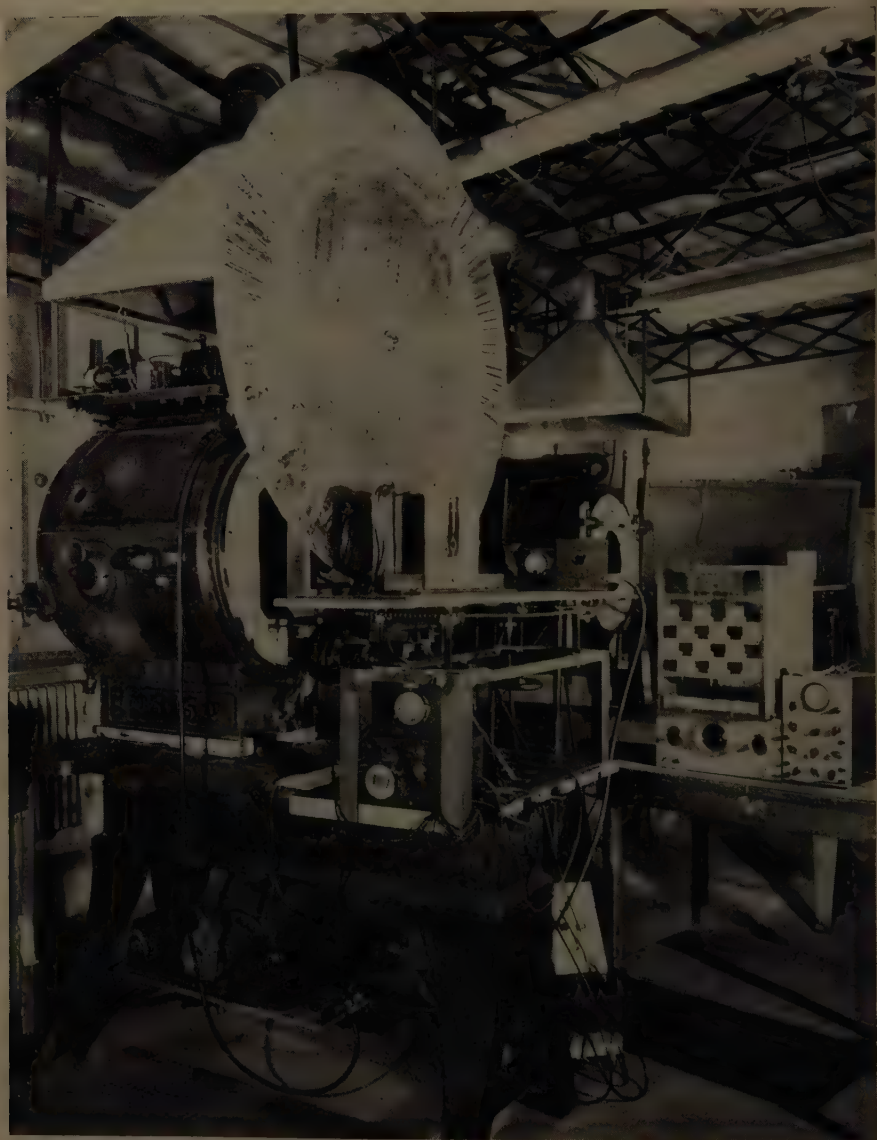


FIGURE 1. University of Rochester carbon arc, showing lathe mount, arc barrel, pulse-shaping and shuttering devices, with exposure port and constant-humidity fabric box.



FABRIC 97 OG (HPM) Contact 6/9/54 735  
 DATE 6/8/54 FIGS # 734

EXPOSURE TIME: 0.5 sec.

cal/cm<sup>2</sup>/sec.

D	H	Q	0	1+ Mild	1+ Sev.	2+ Mild	2+ Mod.	2+ Sev.	3+
M 10 <sup>10</sup>	8.8	4.4	(1)	(9)	(3)	(1)			
11 <sup>3</sup>	9.7	4.85		(8)	(8)	(9)	(3)		
11 <sup>13</sup>	10.7	5.35		(2)	(13)	(8)	(4)	(1)	
12 <sup>7</sup>	11.8	5.9			(4)	(10)	(7)	(7)	
13 <sup>1</sup>	13.0	6.5			(3)	(10)	(6)	(7)	(2)

13<sup>10</sup> 14.3 7.15

(1) (3) (7) (3)

FIGURE 2. Actual summary work sheet. Vertical column, Q, is exposure in cal./cm.<sup>2</sup>; horizontal scale is severity of burn. Each check represents one exposure. These six exposures adequately bracketed the 2 + EE<sub>50</sub>.

sateen interposed in contact with skin requires 5.8 cal./cm.<sup>2</sup> to produce the same result in the same experiment. The "protectivity" of the fabric may conveniently be expressed as a protective index, thus:

$$\frac{2 + \text{EE50 under fabric} = 5.8}{2 + \text{EE50 for bare skin} = 3.8} = 1.53$$

At first, a number of fabric systems that had some military significance were so studied, but the results are of no quantitative importance.

Evidently, the darker the fabric, the less its protectivity; the heavier its weight, the greater its protectivity. Could this be systematized? We had several series of cotton fabrics made up in various shades of white, grey, and black, as well as in various weights. When held in contact with skin, these behaved in a fairly consistent manner, and I was able, after about ten thousand exposures, to formulate their protectivity with this purely empiric (or better, heuristic) expression:

$$P.I. = \frac{k + k'dt^\beta}{1 - R}$$

where  $K$  is a constant = 0.42 and is an expression dependent upon the reflectance and diathermancy of skin;  $K'$  is a constant = 0.056;  $d$  is the weight of fabric in oz./yd.<sup>2</sup>;  $t$  is the exposure time;  $\beta$  is a constant = -0.41; and  $R$  is the specific total reflectance of the fabric to light source used.

A slightly better fit of prediction to fact was obtained by modifying this formula by introducing the factor of fabric transmittance,  $T$ , resulting in the formula:

$$Q_{if} = \frac{At^\alpha + (k + k'dt^\beta)}{(1 - R - T) + T(k + k'dt^\beta)}$$

where  $Q_{if}$  is the radiant energy in cal./cm.<sup>2</sup> incident on the fabric necessary to produce the 2 + EE<sub>60</sub> burn;  $A$  is a constant from bare skin burns, and  $\alpha$  is a second constant from bare skin;  $T$  is the fabric transmittance; and  $\beta$  in this case is equal to -0.25.

By using pulses of energy whose time-irradiance characteristics were virtually the same as those of atomic weapons, a similar expression could be shown to hold, substituting  $w^{b'}$  for  $t^b$  where  $w$  is kilotonnage of the weapon and  $b'$  is a different constant. Since, for any given kilotonnage and height of burst, the caloric yield at any distance from ground zero can be computed, this expression can be used to compute radii of safety from 2 plus burns with 1 layer of cotton fabric in contact with skin.

The simple—or relatively simple—case of 1 layer of fabric in contact with skin very seldom obtains in the clothed human, however. Simultaneously with the above studies, the situation was investigated where the fabric was held an arbitrary 0.5 cm. away from the skin. This, as might be expected, increased the degree of protection, but introduced a further complication in that the fabric rapidly degenerated and sometimes caught fire. Defining the separation factor,

$$S.F. = \frac{2 + \text{EE50 under spaced fabric}}{2 + \text{EE50 under contact fabric}}$$

this ratio was found to vary between approximately 2 and 4 in the fabrics studied, but not in any recognizably systematic fashion.

As a matter of fact, quite early in my studies of a military fabric combination (consisting of an outer layer of green Oxford and an inner layer of tubular knit cotton underwear) used in hot, wet climates, I found some peculiar things. FIGURE 3 shows what happened as the total dose was increased. A paradoxical decrease in burn severity occurred! Further study of this system revealed that

GROSS 2+ BURN THRU 2 LAYERS (H-W)  
AT 5 mm. SEPARATION

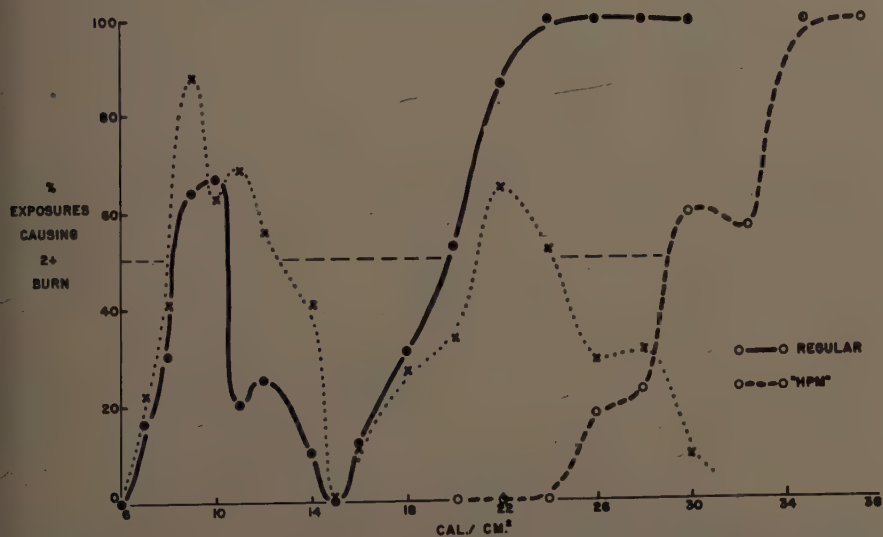


FIGURE 3. Abscissa: exposure in cal./cm.<sup>2</sup> Ordinate: (solid line) percentages of exposures resulting in 2 + burn; (dashed line) same for fireproofed fabric; (dotted line) percentages of exposures resulting in persistent flame and/or glow.

this discontinuity prevailed over a wide range of exposure time and irradiance combinations. Observation of the exposed cloth revealed the fact that the initial burn peak was due to ignition of the fabric, with persistent exothermic reaction producing the burn (FIGURE 4). If, however, larger doses of energy were given, too much of the fabric was destroyed to support combustion, and sufficient of the total incident was consumed in the *endothermic* destruction of fabric completely to protect the underlying skin. Of course, at even higher doses there was no fabric left, and the energy burned the skin by impinging directly upon it.

A very different complex system was also studied to show that such discontinuous behavior can complicate even the fabric-in-contact situation. This system was composed of 2 layers of 9-oz. sateen in contact with skin. Here it was possible to show by thermocouple studies that thermal energy delivered

to the outer lamina continued to travel toward skin after the exposure and there produce damage. However, during very high-intensity, rapid exposures, the energy thus stored could be lost to the system by the destruction of this lamina by endothermic reaction. Again, we had the paradoxical situation where a higher dose produced less burn (FIGURES 5 and 6).

Very extensive studies at NML have shown that flaming of cotton fabric is a complex function involving (at least) humidity, rate of delivery of energy, and lateral flow of air across the fabric. Predictability of behavior in the face of such a complexity of parameters is very low.

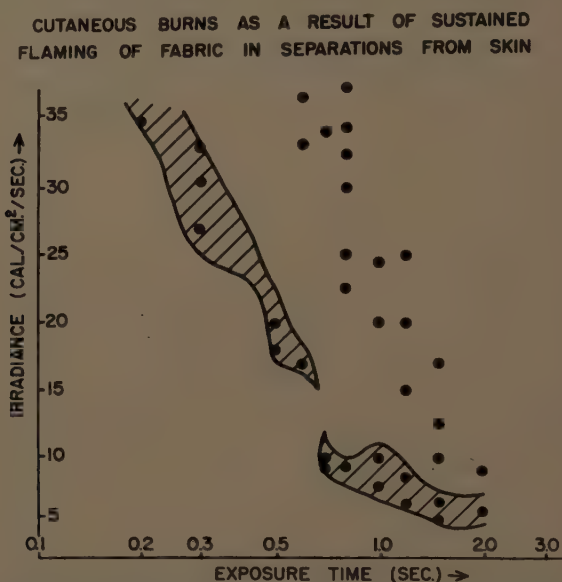


FIGURE 4. Significant burn from flaming fabric: black dots represent average burn of 2 + or more under hot-wet assembly at 0.5-cm. separation. Barred area: exposures causing persistent flaming of fabric. Central empty area: protection of skin by endothermic sacrifice of fabric.

However, the demonstration in the laboratory that ignition may be a significant source of skin burn, and its subsequent confirmation in the field under weapons-test conditions, pointed up the importance of flameproofing of cotton fabrics in the prevention of burns. This led to the development of a still further body of information.

As a preliminary, we must distinguish now between actual ignition of the fabric, with persistent flame and/or glow, and what I have chosen to call the "flare." Under intense irradiance, cotton fabric suspended in nitrogen degenerates rapidly, with production of char and voluminous fumes. The fumes contain carbon particles, tars, water vapor, and flammable gases, in various ratios dependent on the rate of decomposition. Detailed studies of these factors, which began at the University of Rhode Island, Kingston, R. I., were terminated, unfortunately, before a useful body of data was accumulated.

In air, however, such fumes emitting from the exposed face of fabric are



rapidly ignited, and they virtually explode *away from* the surface. They can be shown to contribute little or nothing to the damage of the underlying skin. Some of these fumes, emitted from the back surface of the fabric, condense upon the skin; obviously, they constitute an additional mechanism for thermal transfer from fabric to skin. At the present time, we do not have any secure knowl-

2 LAYERS 9 OZ. SATEEN (OG) IN CONTACT WITH SKIN  
AV. SCORE FOR  $H = 30 \text{ CAL/CM}^2/\text{SEC.}$

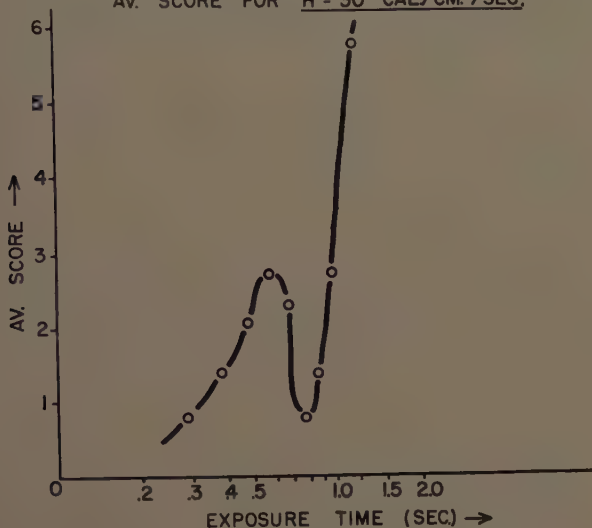


FIGURE 5. Average burn "score" on white pigs with increasing exposure at time at the same irradiance. At 0.8 sec., the outer fabric layer was completely "flashed off."

2 LAYERS 9 OZ. SATEEN (OG) IN CONTACT WITH SKIN  
AV. SCORE FOR  $T = 1.0 \text{ SEC.}$

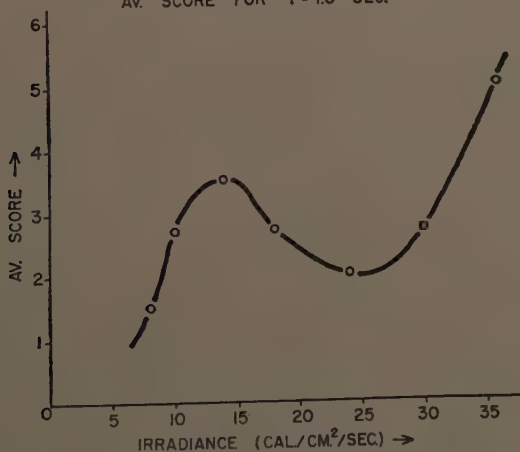


FIGURE 6. Average burn score on pigs under 2-layer system. Exposure time constant at 1.0 sec.; irradiance increased progressively. Note 3 + burns at 14 cal. and only 2 + burns at 24 cal.

edge of how important a function this may be. Nevertheless, this mechanism must be borne in mind when dealing with energy-transfer mechanisms.

To return to more quantitative fields, our animal studies showed beyond doubt that fabric treatment with fire retardants, while it affected protectivity in contact little (or adversely), nevertheless afforded increased protection when separated from skin, as may be seen in FIGURE 7. We were then using fabric treated with HPM, a polymer containing both phosphate and bromine radicals. The fumes ignited, but combustion was not sustained. A further factor was introduced by the toxicity of the unignited fumes, which contained both

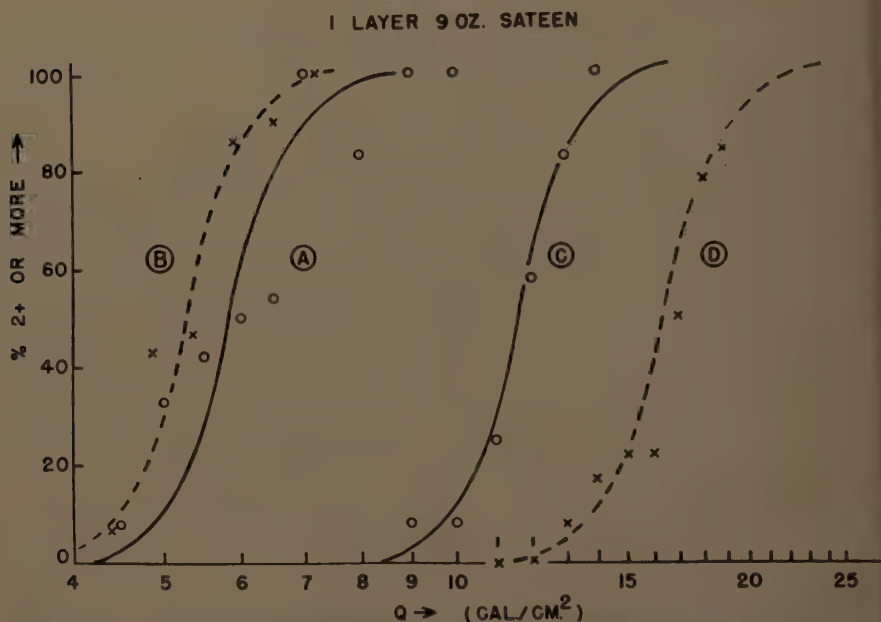


FIGURE 7. Protection enhancement by fire retardant: exposures at 1.0 sec. Curve (A) plain sateen in contact; (B) fire-resistant sateen in contact; (C) plain sateen 0.5 cm. separated; and (D) fire-resistant sateen 0.5 cm. separated. Note significant difference between C and D.

free bromine and acroleinlike substances and were strongly lacrimant and slightly vesicant.

Field experiments in Nevada and in the Pacific have been useful, but not primarily for purposes of quantitation. They have repeatedly demonstrated, as I trust will be realized from this paper, parameters that require definition and complete laboratory investigation, and undiscussed parameters such as exposure area and geometry.

Another such factor, perhaps an obvious one, is the temperature of the skin at the moment an exposure begins. FIGURE 8 shows the result of the first experiment Kelly Berkley and I did, progressively chilling the skin of a pig and observing the burns produced by a certain exposure. Berkley later showed<sup>8</sup>

this effect with statistical rigorousness and avoidance of bias but, to date, there have been no studies of subfabric burns in terms of ambient or skin temperatures.

A few years ago the Naval Material Laboratory demonstrated the effect of fabric moisture upon skin-simulant temperature curves; since that time, it has

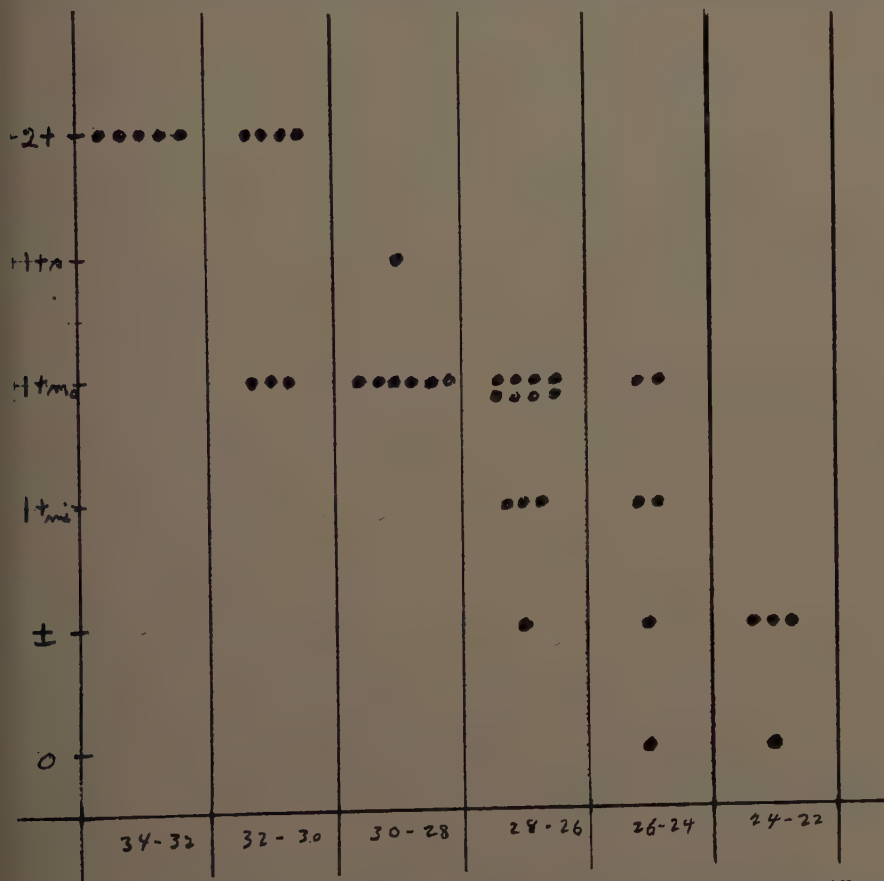


FIGURE 8. Actual summary work sheet. Effect of skin temperature on burns. All exposures 3.5 cal./cm.<sup>2</sup> delivered in 0.5 sec. Abscissa: skin temperature before exposure, °C. Ordinate: severity of observed burn. Each dot represents one exposure. Symbols: 1+ s, severe first degree; 1+ mo, moderate first degree; 1+ mi, mild first degree; ±, early erythema, fading in 12 hours; and 0, no perceptible effect.

been routine at that laboratory and at Rochester to maintain fabric samples at 65 per cent relative humidity for the sake of uniformity. The extremes of moisture and dryness still constitute an almost completely unexplored area, and quite possibly one of significance.

It may be noticed throughout this article that I have never mentioned any studies involving fabrics other than those of cotton. This is because such systematic knowledge as we possess of subfabric burns is derived from data on

cotton. To be sure, fragmentary information has been obtained and reported upon burns sustained beneath all manner of fibers, including wool, nylon, Orlon, Dacron, and vinyl sheets. However, as we have seen, such data are of relatively little theoretical (or practical) value unless a multitude of other parameters are specified and controlled. To date, no such systematic attack has been made upon any fibers other than cotton.

We might begin to recapitulate our present status by a review of those parameters that we have found must be specified (and often suitably varied) before we can make an intelligent estimate of fabric protectivity against intense thermal radiation:

(1) Exposure factors: (a) rate of energy delivery (irradiance); (b) time of exposure; (c) pulsatile combinations of the above; and (d) source temperature (spectral emissivity).

(2) Skin factors: (a)  $K$ ,  $\rho$ ,  $C$ ; (b) diathermancy; (c) reflectance (back-scatter); (d) thickness of various layers; (e) vascular factors; and (f) initial temperature.

(3) Fabric factors: (a) reflectance; (b) transmissivity; (c) thickness (weight per unit area); (d) basic fiber and weave; (e) additive treatment (water or fire retardants); and (f) combinations of fabrics.

(4) Environmental factors: (a) temperature; (b) relative humidity; (c) air flow; (d) area and geometry of exposure; and (e) degree of separation from skin.

We have seen what progress has been made in regard to these various factors up to the present time. A certain degree of quantitation has been accomplished with regard to such physical attributes of fabric as weight, reflectance, and transmittance; and we have defined roughly the contributions of both exothermic and endothermic reactions in fabric.

There is no question in my mind, however, that the fundamental problem that requires understanding at the present time is the relationship between tissue death, temperature, and time. If the physical requirements for irreversible thermal damage could be universally stated, then the remaining problems could be solved by straightforward physicochemical methods, in far less time and at far less expense than by the presently necessary biological and statistical methods. The past ten years have been remarkably fruitful in this rather narrow field of flash burns; it is to be hoped that the next ten will be even more so.

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## HUMAN THERMAL TOLERANCE AND PROTECTIVE CLOTHING

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Human tolerance to heat has been defined for temperatures far above the comfort level, and well above the heat of the desert and tropics. We are concerned with heat that might be termed supraclimatic. Furthermore, we are concerned with tolerance to whole body heating, in which the surface and internal temperatures increase. At these temperatures there is no damage to the surface, as seen in the intense heat of flash fires and bomb blasts, but total damage may occur in the sense of loss of effectiveness, collapse, and even death.

What real situations are there that cause this kind of heat exposure? There are several in industry and several more in military operations; these are briefly presented at the outset to provide a setting for the remainder of this article.

In the Air Force we are greatly concerned with heat in high performance aircraft and, during the re-entry period, heat in ballistic missiles, hypersonic glide vehicles, and spacecraft. The problem has to do with the phenomenon of aerodynamic heating, a process in the boundary layer of still air next to the surface of a vehicle. At high velocities this boundary layer is under greatly increased pressure and high temperature, especially at the leading edges and in front of the nose of the vehicle. The final temperature in the boundary layer at any given velocity and altitude is an equilibrium between the heat of compression on one hand, and on the other, heat radiation to earth and sky and heat conduction along the boundary layer and into the structure. The heat of the aircraft surface can be predicted for these conditions, as shown in FIGURE 1. Here are shown equilibrium temperatures for a point one foot back from the leading edge, as functions of velocity and altitude (Masson and Gazley, 1956). Other references to aerodynamic heating in this mode are made by J. Ross and I. J. Gruntfest.

Heat exposures in industry occur in steel mills, in glass factories, in the ceramics industry, and in paint drying chambers. These are examples of exposure to air temperatures of 140° F. or more, and to radiant heat sources over broad surfaces, at temperatures of several hundred degrees.

In naval operations, men working in the engine rooms of vessels that are under attack may have to stand watch when the room temperature is 130° F. and higher. The ship's ventilators are closed to avoid taking in contaminated air from atomic, bacteriological, or chemical agents.

In all three military services special clothing is worn for decontamination, for protection against toxic fuels, for handling chemical and bacteriological warfare agents, and for protection against low barometric pressure and against cold water immersion. The common feature in all of this special clothing is that they are impermeable to water vapor. The proper physiological response to heat exposure, even if the exposure is mild, is thwarted because sweating has

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no cooling effect when evaporation does not take place. Activity is severely limited in men wearing these garments, from the magnified effects of the heat exposure.

The clothing worn by men who must work in the supraclimatic heat described above must withstand the high temperature. However, I shall discuss this subject later. Let us first review the knowledge of the effects of severe heat exposure on man.

### *Comfort and Compensable Heat Exposure*

The standards for human comfort have been established for some time and are mentioned here only for completeness. An excellent summary of how comfort is defined, and what limits of environment are comfortable, is to be found in the *Heating Air Conditioning Guide* (American Society of Heating and Air-Conditioning Engineers, 1958), which is revised annually.

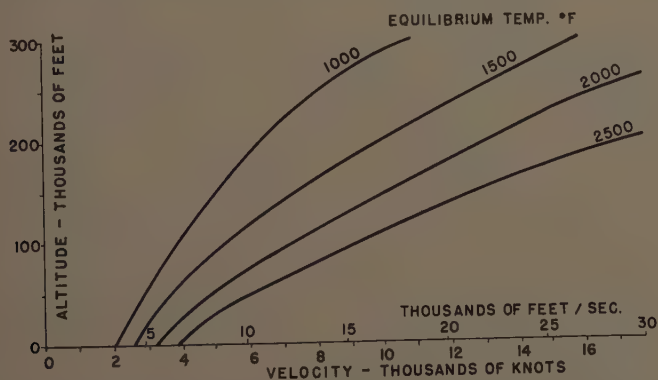


FIGURE 1. Equilibrium temperatures on the surface of a fast moving vehicle at a point one foot back from the leading edge, plotted as functions of velocity and altitude. Reproduced by permission of the Institute of Aeronautical Sciences, New York, N. Y.

Just beyond the comfort zone, on the warm side, there is a set of environmental conditions that can be met by the normal thermoregulatory responses (as long as they are not hindered by special clothing). The responses are: dilation of the blood vessels in the skin, to increase the transfer of internal heat to the surface, where it can be lost, and sweating, to cause loss of heat by mass transfer, or evaporation.

When the heat exposure is mild, and it is not aggravated by impermeable clothing, a man can compensate for it through his physiological responses. This heat exposure lies in the compensable range and leads to difficulty only if quite prolonged, for many hours, owing to fatigue.

Since the level of heat involved in comfort conditions and compensable heat exposure is familiar to everyone and causes no particular textile problem, we proceed at once to the more challenging area of noncompensable exposures.

### *Noncompensable Heat Exposure*

There are heat exposures that are too severe for physiological responses to handle. These are the supraclimatic levels of heat described earlier. The re-

sponses of vasodilation and profuse sweating are insufficient to maintain a steady body temperature, and the exposure is necessarily time limited.

The rate of rise of body temperature varies, under these conditions of heat, with the severity of the heat load. If the rise is slow but continual, and the slope is shallow because of the effect of physiological responses, we have what the late Craig Taylor at the University of California at Los Angeles called the "quasi-steady state." If the rate of rise is fast, the time limit is much shorter.

Heat loads must be complexly described because so many factors are important. Not only do we need to know air temperature, wall temperature, and humidity: we must also include in the description of heat load the air motion, air density, presence of solar radiation, the clothing in terms of its insulation value, its surface reflectivity, and its permeability to water vapor and, finally, the man's activity level, which determines the size of the contribution of his internally-produced metabolic heat. This unwieldy array of variables prevents us from devising any simple "heat-load-o-meter" or indeed from making any simple formula for predicting the effect of the heat load.

What is usually done is to use the man as the biological indicator of the effect of any given heat load. In other words, one must reproduce the conditions of interest, put a man in, and measure his responses to know how bad the exposure is.

We shall not describe here the various ways of describing physiological strain. Most indices of strain rely on one or more of the three principal measurements—heart rate, rectal temperature, and rate of sweat production.

The upper limit of physiological strain is reached at either the point where the man's function is impaired, which is called the performance limit, or where the man is overwhelmed by the heat exposure and is on the verge of collapse, the physiological tolerance limit. We have had considerable experience now with the physiological tolerance limit, both at the University of California and at the Aero Medical Laboratory. The performance limit is harder to measure under artificial conditions, but we use a rule of thumb, based on limited measurements, that the performance limit is reached in about three fourths of the time required to reach the physiological tolerance limit (Blockley *et al.*, 1954).

Let me describe more fully the end point called the physiological tolerance limit. At a late stage in an experiment involving a noncompensable heat exposure, we observe in the subject a high and rising rectal temperature, a strong and rapid pulse, a flushed, dry skin (where previously there had been copious sweating), some increase in the rate and depth of breathing, and a growing restlessness and inability to fix attention on any task. This man is on the verge of collapse. By experience the medical observer can tell just when to stop the experiment, knowing that another five minutes of exposure will bring unconsciousness. The subject is in a state of impending heat stroke.

Notice the term heat stroke rather than heat prostration or heat exhaustion. The terminal condition in these severe experiments resembles closely the classical signs of clinical heat stroke, not the signs of prostration where the skin is cool and moist, the pulse rapid but weak, and the person fainted but easily aroused. In our subjects the only way to reverse the condition is to stop the experiment and begin active cooling of the body surface. We have recently measured cardiac output during some of these exposures to find that the heart



responds maximally to the heating by an increase in rate, and a maintenance or increase in stroke volume, right to the end of the experiment. In contrast, the person with heat prostration is in near shock, with a fast thready pulse and very likely a low cardiac output from a decreased stroke volume.

The internal temperature of the man in this state of impending heat stroke is at about 102° F. This is of course not alarmingly high, when taken alone. An exercising man in heat is expected to develop an internal temperature of 104° F. before having to stop. Clinical patients with febrile disease often achieve temperatures, measured rectally, of 106° F. What is the difference in these three situations?

Actually, it appears that there may be little difference at all, that all three cases are reaching the same level before serious trouble from hyperpyrexia develops. If one takes the mean body temperature rather than the rectal temperature alone, a very significant thing happens. The febrile patient, the exercising man, and the resting subject in severe heat all reach the same mean body temperature at tolerance.

Mean body temperature is derived from measurements of both the temperature at the body surface and from an internal temperature measurement. Skin temperatures, and either rectal or rectal plus esophageal temperatures are commonly measured in a physiology laboratory. The skin temperature times 0.33 and the internal temperature times 0.67 are added together to give the mean body temperature (Burton, 1935).

When mean body temperatures are taken for our subjects who are sitting still in a hot chamber, the high mean skin temperature (up to 104°) brings up the mean body temperature to about 103° F. on the average. In the case of the exercising man, his rather high mean skin temperature of about 97° F. brings the mean body temperature again to about 103° F. In fever, the effect of the high rectal temperature is lessened in calculating mean body temperature by the fact that the skin temperature is not extraordinarily high. It appears that in high fever the mean body temperature would also approach 103° F. The mean body temperature is the common denominator for these diverse conditions (Webb and Polte, 1958).

A rather thorough study has been made of tolerance limits under many different conditions for the temperature range from comfort to about 250° F. We can predict tolerance times for much of this range either in terms of performance or collapse. The major work, done at the University of California is summarized in a technical report from Wright Air Development Center, Wright-Patterson Air Force Base, Ohio (Blockley, McCutchan and Taylor, 1954). Additional work with impermeable clothing has been published (Veghte and Webb, 1957). This information, together with the newer work on ventilated clothing and that on slow heat pulses, has considerable practical importance in aviation.

### *Ventilated Clothing*

All of the tolerance limits in heat are drastically altered when the subject is wearing a ventilating garment, the primary means of protection against heat. In addition to providing excellent protection against supraclimatic heat exposure, ventilated clothing solves the difficult problem of impermeable clothing in heat. The impermeable layer is circumvented by introducing moving air

under the clothing. Fetcher and his co-workers (Fetcher, Rappaport, Hall and Shaub, 1949) defined the requirement with some precision, and a number of air distributing systems have now been devised for the purpose.

The best device for delivering and distributing ventilating air in clothing was developed at the Air Force Aero Medical Laboratory, Wright Air Development Center (Mauch, 1955), and since then it has been improved and applied to many



FIGURE 2. The Air Force Ventilating Garment type MA-3 as worn by a subject dressed in a light coverall and an outer insulating coverall. Note that the ventilation garment is worn under and between other layers of clothing.

types of clothing (Webb and Klemm, 1958). A photograph of a late model ventilating harness is shown in FIGURE 2.

In the ventilating device, air is delivered through a central hose to a space between two layers of plastic film. Spreading laterally between the layers, the supply air can escape only through tiny pinholes located over the inner film, but not the outer. After moving against the undergarment a short distance, the heated and moistened air now can escape by coming out through the larger holes, visible in the photograph, which traverse both layers of plastic, and so to an outlet to be carried away.

A complete ventilated clothing assembly must contain a number of functional layers in order to operate effectively. Air must be brought in, evenly distributed

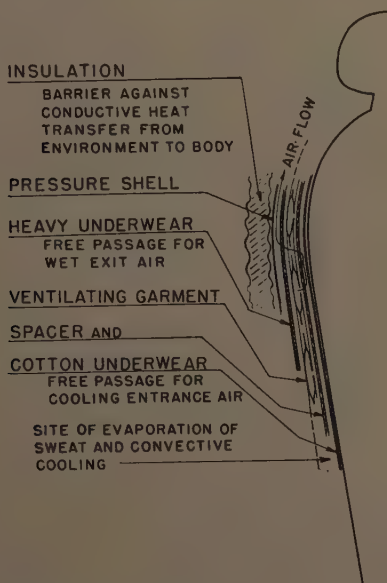


FIGURE 3. The construction of a complete ventilated assembly in a full pressure suit. From Webb and Klemm, 1958.

over a large body area, given a good chance to pick up water vapor, and be conducted away without local blockages to flow. Furthermore, a well designed clothing assembly uses passive insulation and counterflow principles to achieve maximum effectiveness of convective cooling. Although many common types of clothing do not need elaborate measures to insure all these effects, some special clothing does require a whole series of air layers to make the system work. Such an arrangement is shown in cross-section in FIGURE 3, which is a diagram of the layers in a ventilated full pressure suit.

What effect has ventilation in a severe heat exposure? This might best be visualized by looking at the physiological data from two similar experiments, in one of which the subject is ventilated. In FIGURE 4 we see somewhat diagrammatically, the pulse response, increase in internal temperature, and rate of sweat production for two subjects. The nonventilated man reaches the physiological tolerance limit in one hour and his physical condition is very poor. He

has reached the physiological tolerance limit described in the previous section. By contrast, the ventilated subject has produced sweat, which has been largely evaporated, and his pulse and rectal temperature have found a new level, which can be maintained for three hours. This subject has been stressed, but is still quite well able to perform at the end of the run.

There is a good deal of experimental work now published on the effects of ventilation, and on the importance of rate of flow of supply air, its temperature and humidity, and on the effects of clothing, altitude, activity, and so forth. This work has been done at the Navy's Air Crew Equipment Laboratory (Greider and Santa Maria, 1957; Libber, Santa Maria, and Viccaro, 1958), at the Air Force Aero Medical Laboratory (Mauch, Hall and Klemm, 1955;

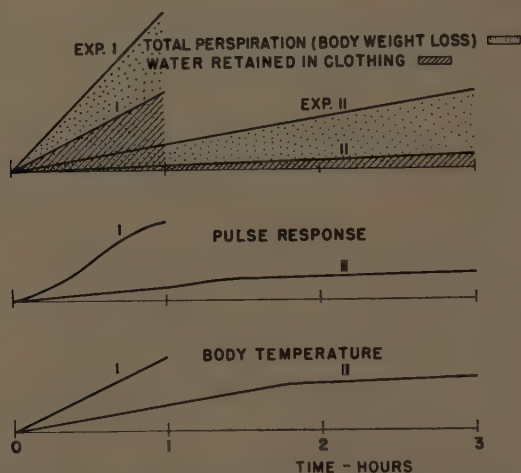


FIGURE 4. The effects of heat exposures in man both without ventilation (experiment I) and with ventilation of the clothing (experiment II). Chamber temperature is 160° F., wall and air, and the air is dry. In both experiments the subject wears a heavy suit which is covered by an impermeable shell, the antiexposure suit assembly, with an added Air Force ventilating garment. Ventilating air in experiment II is delivered at the rate of 10 cfm. and has a temperature of 45° F. at the suit inlet. From Webb, 1956.

Webb, 1956; Webb and Veghte, 1956) and at the University of California (Skilling, McCutchan, and Taylor, 1956). Hopefully, there will soon be enough experience with ventilated assemblies in heat to enable one to predict tolerance limits for many combinations of environmental and ventilatory variables.

The important thing to realize in the context of this discussion is that with present day techniques in ventilated clothing, a man may be able to stay in an extremely hot environment for hours and remain quite able to perform. The outside surface of his clothing during this time would reach a high temperature, while he remained relatively cool within.

#### *Temperature Transients*

A new field of investigation is beginning to receive attention by physiologists. This concerns man's tolerance to temperature transients, usually abrupt and



extreme changes either in one direction, or up and down. This sort of problem is important in the coming age of space flight. A fast moving vehicle re-entering the earth's atmosphere may expose the man to a rapidly rising temperature as it slows down, then it cools down rather quickly.

We have just begun to attempt this sort of experiment in a small box-shaped chamber, a four-foot cube, which is heated by banks of radiant heat lamps. An example of the sort of heat exposure we are interested in is shown in FIGURE 5. This might be termed a slow heat pulse (as opposed to the rapid heat pulse of a bomb blast). The one illustrated was chosen as representing the type of heating that could occur in an aircraft cabin during supersonic flight, if the

#### HEAT PULSE OVEN

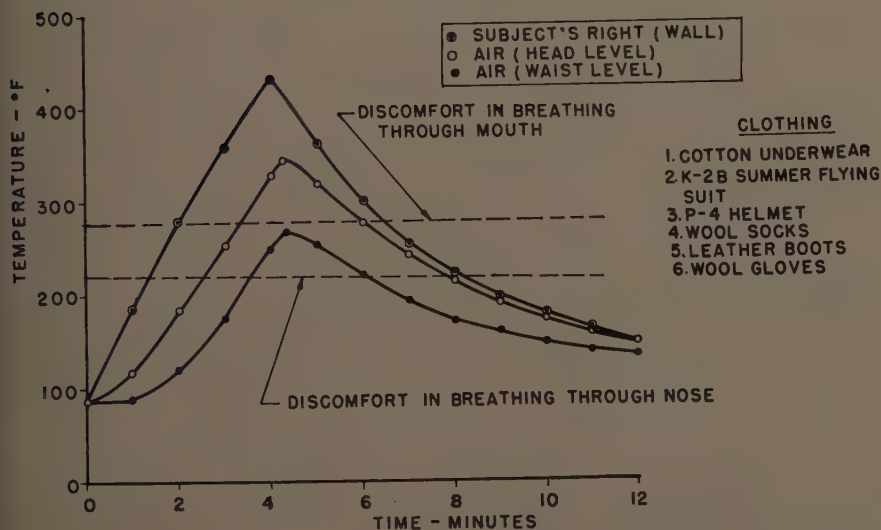


FIGURE 5. Example of conditions produced for study of tolerance to slow heat pulses. This condition is tolerable for a lightly clothed man, sitting and engaged in light activity.

cooling system suddenly failed. As shown, this particular slow heat pulse is quite tolerable by a man protected only in light flying clothing, with gloves, helmet, and oxygen mask. Other shapes of curves and other rates of change are to be tried.

#### Precooling

One final topic should be brought in briefly to add to the argument for high-temperature clothing. This is the new subject of extending human thermal tolerance by prior body cooling. We have reviewed man's tolerance to supraclimatic heat, seen how ventilated clothing extends this tolerance greatly, and had a glimpse of how extreme a temperature one can manage in a brief, transient period of heat. A method of preparing a man for a long stay in an intolerably hot environment is precooling.

Assume that the body is a tank of water—that its physiological responses are

not too effective in extreme heat. This body can be heated only to a certain maximum temperature, so that if one cools the tank just before a heat exposure, it should take longer to reach the maximum temperature, or tolerance limit. This has been tested by cooling test subjects and then exposing them to a high level of heat (Veghte and Webb, 1958). A man's limit for a 160° F. chamber while wearing just a suit of light underwear is about 60 min. If his average body temperature is lowered by 4° F., he can withstand the heat for almost 120 min. Furthermore, for the first 20 min. after entering the heat, the precooled subject does not even sweat or feel uncomfortable. This trick might find uses in situations where a brief exposure to high temperature is anticipated.

### *Summary and Conclusion*

Man can well tolerate temperatures of 200°, 300°, 400° F., and perhaps higher for minutes and hours, depending on the heat load and the degree of protection supplied. Excellent protection in the form of clothing is available through the proper use of ventilation, insulation, and reflective coatings. Tolerance can be further extended by cooling off just prior to an expected heat exposure.

The result of this knowledge may be that clothing technology will need to advance to meet the special problems of high temperature in the clothing itself. Fabrics and joinings in the outer layer may have to retain strength despite a several hundred degree temperature. Gloves for handling hot surfaces, elimination or covering of metal closures and snaps that conduct heat straight to the skin, and special foot-gear with low thermal conductivity are all problems that are already troublesome in our experimental work. The new physiology of man's tolerance to supraclimatic heat poses a new challenge to the clothing industry.

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# THERMAL STABILITY, FLAMMABILITY, AND MELTING CHARACTERISTICS OF TEXTILE SUBSTRATES\*

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## FIBERS AND THEIR BLENDS

### *Introduction*

A knowledge of the behavior of textiles at elevated temperatures has become increasingly important in many industrial and military applications.<sup>1-5</sup> The products of the thermal decomposition of fibers and the mechanisms of their thermal degradation are factors that must be considered in the solution of the problem of providing effective flame and thermal protection in clothing.<sup>6-8</sup> In order to determine the behavior of textile fiber-forming polymers of different chemical compositions at high temperatures (400 to 1000° F.) 18 different natural, regenerated, derivative, or synthetic fiber types (TABLE 1) were studied. The materials represented a cross section of commercially available fibers and were used in bulk form. A series of 50/50 blends of these fibers with cotton was prepared in order: (1) to study the behavior of fiber blends at high temperatures; (2) to compare the behavior of the blends with that of the individual components; and (3) to elucidate the mechanisms of interactions at elevated temperatures of chemically different fibers in a blend.

The thermal responses of nylon and cotton blended in the proportion 10/90, 25/75, 50/50, 75/25, and 90/10 were also determined so as to investigate the effect of concentration of the admixed component (nylon) on the behavior of the blend (nylon/cotton) at high temperatures.

### *Experimental*

All fiber types except Vinyon-HH were Soxhlet extracted with carbon tetrachloride, rinsed in hot water, and air dried for 48 hours prior to use. The blends were prepared on a laboratory-size mechanical blender.<sup>9</sup> Two-hundred-and-fifty-milligram samples, shaped in small balls, were pyrolyzed on a 3 × 3-inch piece of 5-mil aluminum sheeting in an aluminum-lined muffle furnace. The floor of the furnace was covered with a corrugated aluminum platform. These precautions were taken in order to minimize temperature variations within the furnace. The previously weighed specimens were placed in the furnace for 2 min., removed, and reweighed after a 24-hour conditioning period. The temperature range of the studies was 400 to 1000° F.; data were taken at intervals of approximately 50° F.

### *Data and Results*

*Melting characteristics.* The fibers could be classified into two groups by an examination of the residues after pyrolysis:

\* The work described in this paper was supported by the Clothing and Textile Division, United States Naval Supply Research and Development Facility, Brooklyn, N. Y., under Research Contract No. N140 (132) 57442B, and subsequent modifications.

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(1) Fibers that carbonized and decomposed without melting, leaving a brittle char residue: cotton, Fortisan, silk, Vicara, vicuña, viscose, and Zefran. This type of behavior is illustrated in FIGURE 1 by cotton.

(2) Fibers that melted and formed a bead prior to decomposition, leaving a hard or brittle char residue: acetate, Acrilan, Arnel, Dacron, Darvan, Dynel,

TABLE 1  
CLASSIFICATION OF FIBER TYPES

<i>Cellulosic</i>	
Natural	cotton
Derivative	acetate, Arnel
Regenerated	Fortisan, viscose
<i>Protein</i>	
Natural	silk, vicuña
Regenerated	Vicara
<i>Synthetic</i>	
Polyamide	nylon, nylon-6
Polyester	Dacron
Vinyl	Vinyon-HH
Acrylic	Acrilan, Darvan, Dynel
	Orlon, Verel, Zefran



FIGURE 1. Cotton; temperatures °F.

nylon, nylon-6, Orlon, Verel, Vinyon-HH. The behavior of nylon is shown in FIGURE 2. In contrast to the behavior of the rest of the fibers, Vinyon-HH intumesced into a solid foamlike structure between 600 to 800° F.

The melting behavior of the 50/50 blends with cotton was different from that of their synthetic-fiber component. The beadlike residue of the synthetic fiber was eliminated; its melt was absorbed onto the surface of the cotton fibers. In the nylon-cotton series there was no formation of a bead even at the highest nylon content: 90 per cent (FIGURE 3). Blending with cotton is, therefore, a



method of eliminating the bead that results when synthetic fibers are heated to high temperatures.

*Thermal stability.* Percentage loss in weight was used as a measure of thermal stability.<sup>10, 11</sup> These data for the fibers are shown graphically in FIGURES 4a, b, and c.



FIGURE 2. Nylon; temperatures °F.

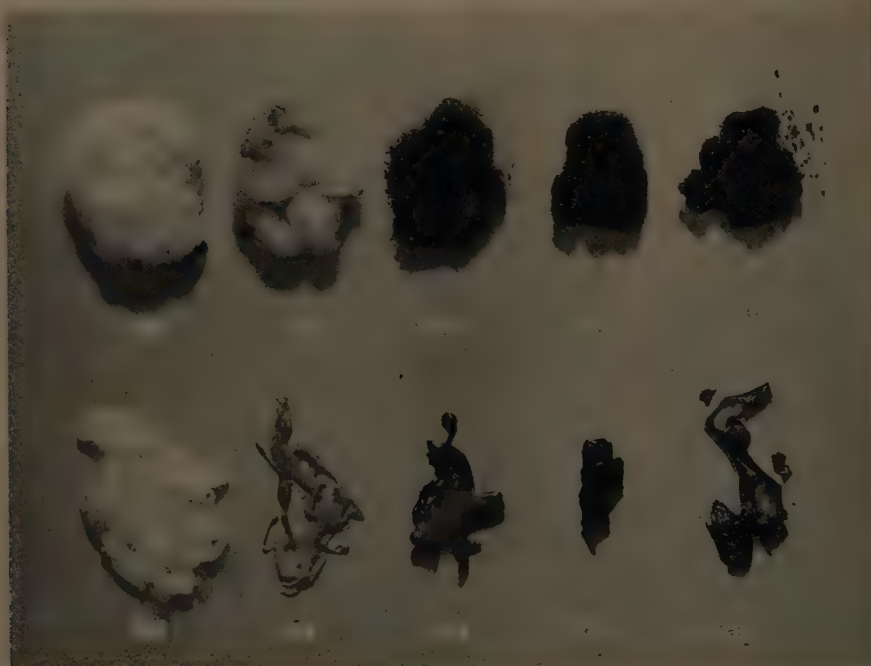


FIGURE 3. (*Upper*) nylon-cotton, 90/10; (*lower*) nylon, temperatures °F.

With regard to the thermal behavior of the three natural fibers, vicuña and silk behave similarly and show no abrupt changes in rate of decomposition with temperature; cotton shows an abrupt acceleration in rate of decomposition at 700° F. As a consequence, cotton is more thermally stable below 700° F. than vicuña and silk. Above 700° F. cotton is less stable. Silk is the most thermally stable of these three fibers above 800° F.

The data for cellulosic fibers (FIGURE 5) show that the regenerated varieties (Fortisan and viscose) are less thermally stable than cotton; the derivative acetates are more stable as measured by percentage weight loss. The triacetate (Arnel) is more stable than the diacetate (acetate).

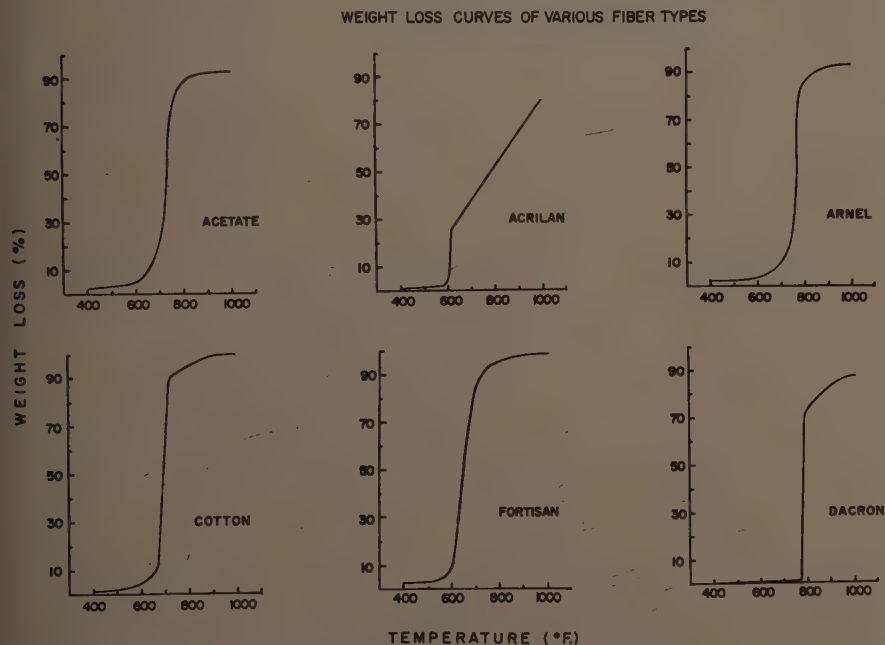


FIGURE 4a.

With regard to the synthetic fibers (Acrilan, Dacron, Darvan, Dynel, nylon, nylon-6, Orlon, Verel, Vicara, Vinyon-HH and Zefran), varying degrees of thermal stability are evident. At temperatures above 800° F., Dynel, Orlon, and Verel are the most stable.

Acrilan, Dynel, Orlon, Verel, and Zefran are similar chemically, having as their major component acrylonitrile or acrylonitrile co-polymerized with vinyl acetate or vinyl chloride. The observed differences in thermal stability can be related, therefore, to either: (1) differences in the chemical nature of the copolymer; or (2) differences in the ratio of the two components of the polymer. The fibers Acrilan, Darvan, and Vinyon-HH contain vinyl acetate as one component. The differences in their thermal behavior can be related to the effects of the decomposition products of the second component.

The thermal behavior of the fibers and of the blends may be compared by two

## WEIGHT LOSS CURVES OF VARIOUS FIBER TYPES

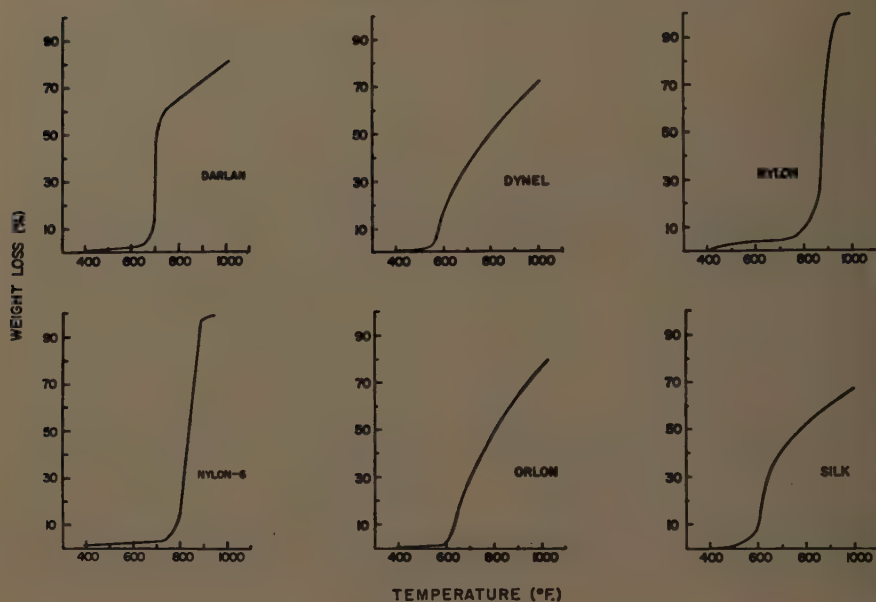


FIGURE 4b.

## WEIGHT LOSS CURVES OF VARIOUS FIBER TYPES

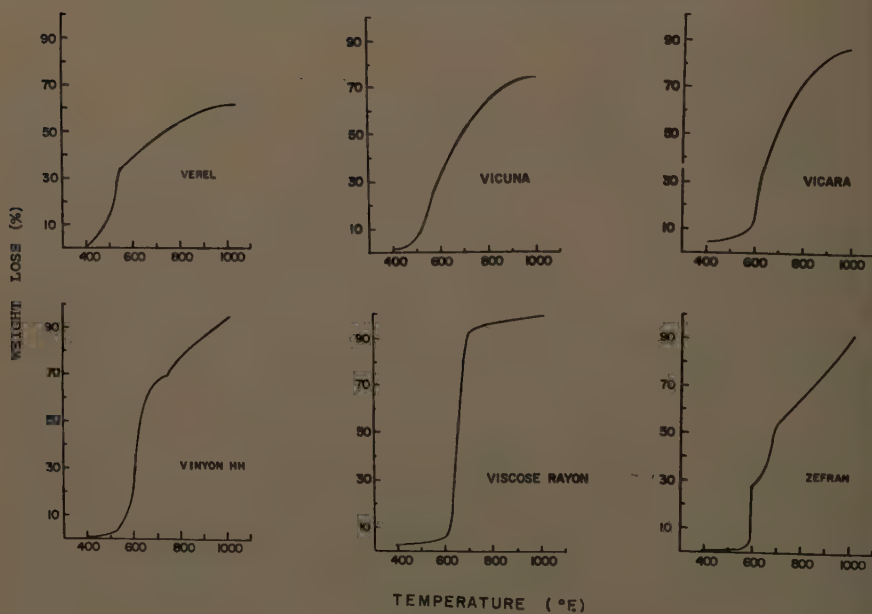


FIGURE 4c.

criteria: (1) weight loss at a temperature within the range of study (700° F.); and (2) the temperature at which 50 per cent decomposition has occurred. These data for the fibers are listed in TABLES 2 and 3.

The loss-in-weight data for the 50/50 blends are shown graphically in FIGURES 6*a*, *b*, and *c*. The calculated curves in these figures were obtained by averaging, at every 50°, the loss-in-weight data for the individual components of the sys-

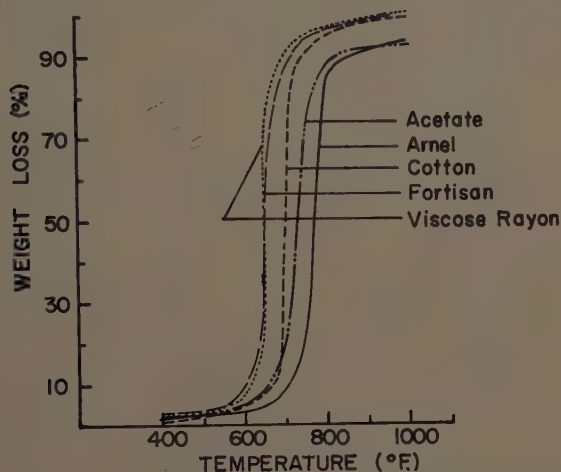


FIGURE 5. Weight-loss curves of cellulosic fiber types.

TABLE 2  
DECOMPOSITION AT 700° F. OF FIBER TYPES

Weight-loss percentages	Fiber types
10	Dacron, nylon-6, nylon, Arnel
20	
30	
40	acetate, Darvan, Orlon
50	Dynel, Acrilan
60	silk, Verel
70	vicuña, Vicara, cotton
80	Vinyon-HH
90	Fortisan
100	viscose

tems. The loss-in-weight data for the nylon-cotton series are plotted in FIGURE 7. In this case the calculated curves were obtained by weighting the decomposition values for 100 per cent nylon and 100 per cent cotton according to the composition of the blend.

As shown from the weight-loss data at 650° F. (TABLE 4), the 50/50 blends in general decomposed to a greater extent than the pure cotton. However, a spectrum of stability values was obtained: the nylon-cotton blend was the most stable; the Vinyon-HH-cotton blend was the least stable by this criterion. The

experimental 50 per cent decomposition temperatures for the blends are given in TABLE 5, along with calculated values. The experimental 50 per cent decomposition temperatures were lower than the calculated values for all of the blends except silk-cotton. The blends, with this one exception, were less stable

TABLE 3  
FIFTY PER CENT DECOMPOSITION TEMPERATURES OF FIBER TYPES

Fiber type	Temperatures (°F.)
acetate.....	730
Acrilan.....	785
Arnel.....	765
cotton.....	695
Dacron.....	785
Darvan.....	710
Dynel.....	800
Fortisan.....	655
nylon.....	885
nylon-6.....	840
Orlon.....	810
silk.....	775
Verel.....	790
Vicara.....	685
vicuña.....	695
Vinyon-HH.....	630
viscose rayon.....	660
Zefran.....	690

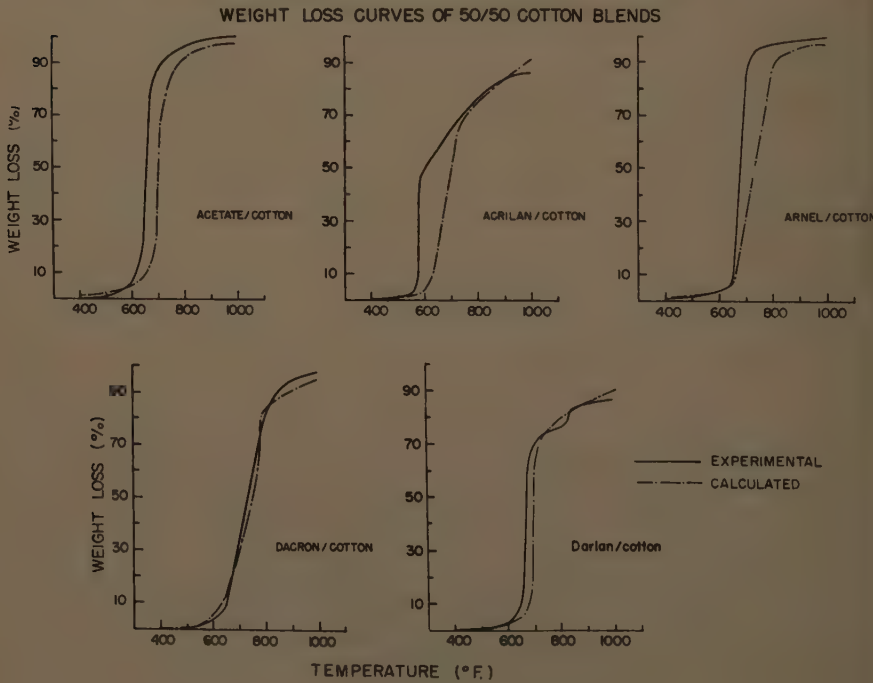


FIGURE 6a.



# WEIGHT LOSS CURVES OF 50/50 COTTON BLENDS

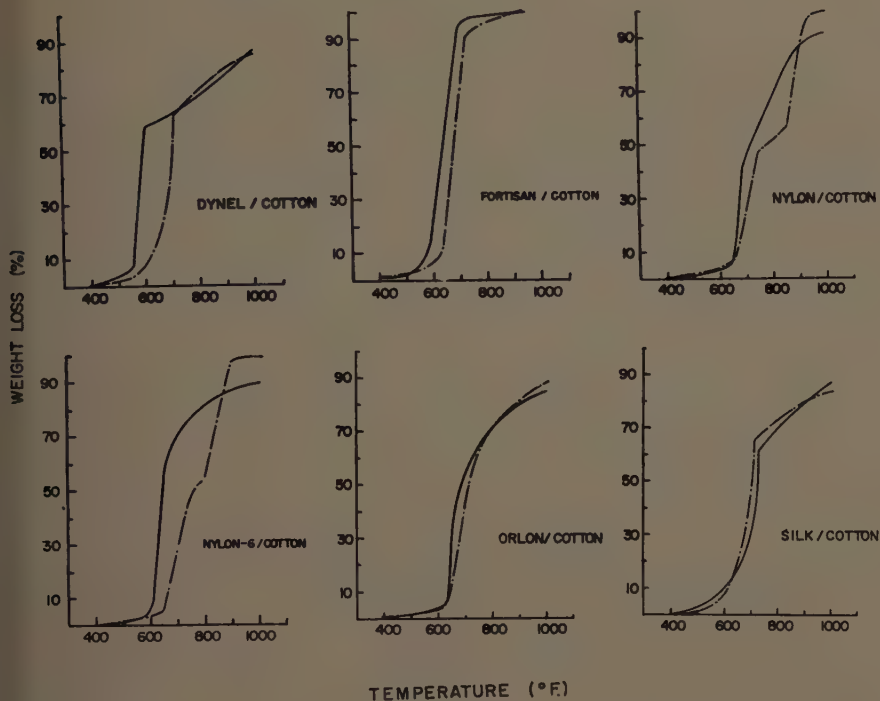


FIGURE 6b.

# WEIGHT LOSS CURVES OF 50/50 COTTON BLENDS

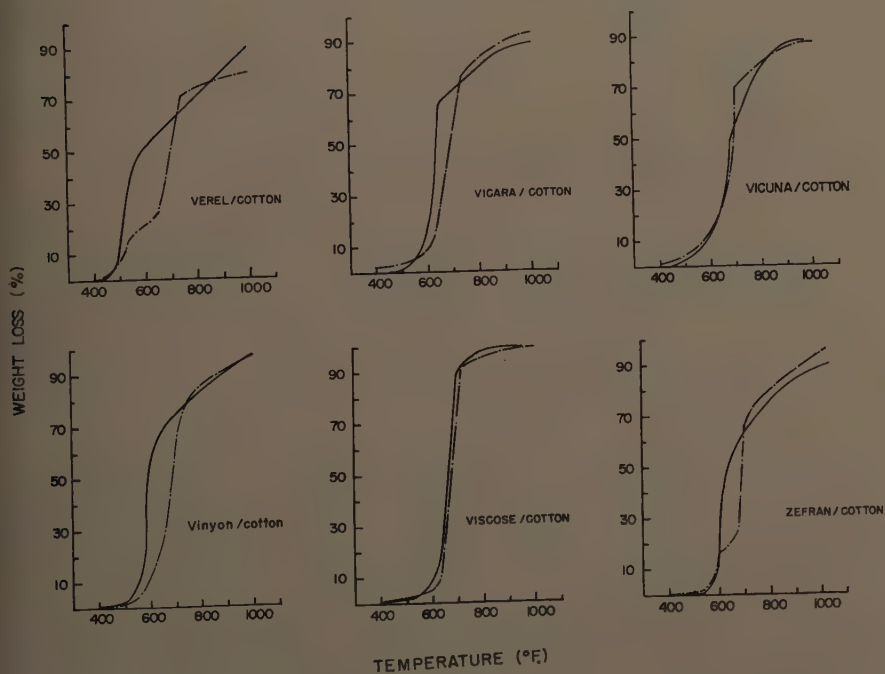


FIGURE 6c.

thermally than predicted. Two types of behavior were noted: (1) a 50 per cent decomposition temperature below that of either component (acetate, Acrilan, Arnel, Darvan, Dynel, Fortisan, Orlon, Verel, Vicara, vicuña, Vinyon-HH, viscose, Zefran); and (2) a 50 per cent decomposition temperature between those of the individual components (Dacron, nylon, nylon-6, silk). The difference between the experimental and calculated 50 per cent decomposition temperatures may be used as an index of chemical interactions between the decom-

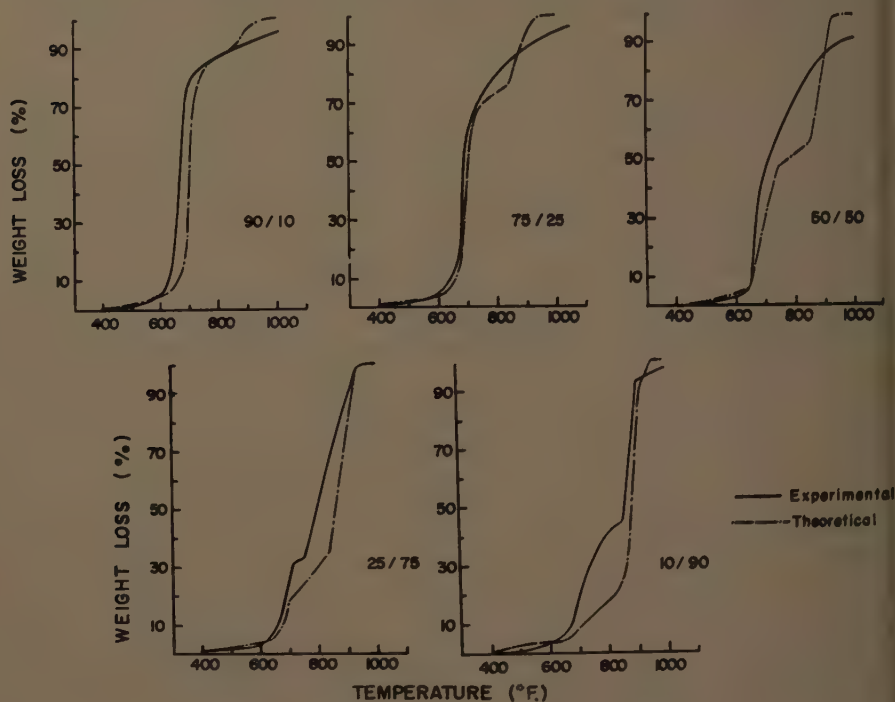


FIGURE 7. Weight-loss curves of cotton-nylon blends.

TABLE 4  
DECOMPOSITION AT 650° F. OF 50/50 BLENDS WITH COTTON

Weight-loss percentages	Second component
<10	nylon, Arnel, Dacron
20	Darvan, vicuña, silk
30	
40	acetate, orlon, viscose
50	
60	nylon-6, Zefran, Fortisan, Verel, Acrilan
70	Dynel, Vicara, Vinyon-HH
80	
90	
100	

One hundred per cent cotton = 8%.

position products of the components of the blends and the constituents of the mixture. The larger the difference, the more pronounced the effect. This situation is analogous to the catalytic effects noted in the decomposition of polymers in the presence of various gases.<sup>12-14</sup> The largest difference (120° F.) was noted in the case of the Verel-cotton blend.

TABLE 5  
FIFTY PER CENT DECOMPOSITION TEMPERATURES FOR 50/50 BLENDS WITH COTTON

Second component	Experimental	Calculated	Calculated minus experimental
	(°F.)	(°F.)	(°F.)
acetate.....	660	705	45
Acrlan.....	605	705	100
Arnel.....	675	725	50
Darvan.....	670	700	30
Dynel.....	595	705	110
Dacron.....	730	750	20
Fortisan.....	640	680	40
nylon.....	720	775	55
nylon-6.....	700	760	60
Orlon.....	685	720	35
silk.....	725	700	-25
Verel.....	585	705	120
Vicara.....	640	695	55
vicuña.....	675	700	25
Vinyon-HH.....	590	685	95
viscose.....	655	680	25
Zefran.....	640	695	55

TABLE 6  
FIFTY PER CENT DECOMPOSITION AND MINIMUM IGNITION TEMPERATURES  
OF NYLON-COTTON BLENDS

Nylon-cotton ratio	Fifty per cent decomposition temperatures		Minimum ignition temperature
	Experimental	Calculated	
	(°F.)	(°F.)	(°F.)
0/100	695	695	755
10/90	670	700	775
25/75	695	710	820
50/50	720	770	865
75/25	795	865	885
90/10	855	880	895
100/0	885	885	905

The thermolysis data indicate that the 50/50 blends of cotton with the cellulosic fibers are less stable thermally than 100 per cent cotton. The cotton blend with Arnel is more stable than the corresponding blends with acetate, viscose, or Fortisan. The blends of the protein fibers (Vicara, vicuña and silk) with cotton show greater thermal stability than 100 per cent cotton at temperatures greater than 675° F. The blend with silk is more stable thermally than the corresponding blends with wool or Vicara.

Similar data for nylon-cotton blends (TABLE 6) indicate these blends also had 50 per cent decomposition temperatures significantly lower than the calculated values. As the amount of nylon in a nylon-cotton blend was increased, the 50 per cent decomposition temperature of the blend increased. The difference between experimental and calculated 50 per cent decomposition temperatures did not change regularly with blend ratio.

*Flammability behavior.* In TABLE 7 are given the temperatures at which each fiber first flamed and the temperature below which no flame resulted. The average minimum temperature for ignition for all fibers is approximately 860° F., which is 115° F. higher than the average 50 per cent decomposition temperature. More than 80 per cent of the material decomposes before ignition occurs. The fiber types may be divided into 3 groups according to flam-

TABLE 7  
FLAMMABILITY OF FIBER TYPES

Fiber type	No flame	Flame
	(°F.)	(°F.)
acetate.....	820	825
Acrilan.....	890	900
Arnel.....	820	825
cotton.....	745	755
Dacron.....	905	920
Darvan.....	900	920
Dynel.....	1000	
Fortisan.....	795	800
nylon.....	885	895
nylon-6.....	835	850
Orlon.....	855	865
silk.....	1000	
Verel.....	1000	
Vicara.....	865	880
vicuña.....	950	960
Vinyon-HH.....	1000	
viscose.....	795	810
Zefran.....	800	825

mability behavior. Fibers in Group 1 (acetate, Arnel, cotton, Fortisan and viscose) have an average minimum ignition temperature of 810° F. and an average weight loss prior to ignition of 90 per cent. Fibers in Group 2 (Acrilan, Dacron, Darvan, nylon, nylon-6, Orlon, Vicara, vicuña, and Zefran) have an average minimum ignition temperature of 875° F. and an average weight loss prior to ignition of 65 per cent. Fibers in Group 3 (Dynel, silk, Verel and Vinyon-HH) did not ignite within the temperature range studied. The average loss in weight of these fibers at 1000° F. is 74 per cent. TABLE 8 lists similar data for the 50/50 blends with cotton. The average minimum ignition temperature of the blends is 805° F., which is 145° F. higher than the 50 per cent decomposition temperature. About 90 per cent decomposition of the blend has occurred by the time this temperature is reached. In all cases the minimum ignition temperature of the 50/50 blend is significantly higher than that of the cotton and lower than that of the second component. The maxi-

imum effect is realized in the vicuña-cotton blend, where the minimum ignition temperature of the blend is 100° F. higher than that of 100 per cent cotton.

As the amount of nylon in a cotton-nylon blend is increased, the minimum temperature for ignition also increases and, as shown in TABLE 6, the 50 per cent decomposition temperature is also increased. Therefore, by changing the components and proportions of the constituents of a blend, the flammability, melting, and thermal properties of the system may be altered.

### Conclusions

The thermal behavior, flammability, and melting characteristics of 18 fiber types of different chemical composition were studied. The melting behavior of the fibers could be classified into two types: (1) decomposition without melt-

TABLE 8  
FLAMMABILITY OF 50/50 BLENDS WITH COTTON

Second component	No flame	Flame
	(°F.)	(°F.)
acetate.....	760	775
Acrilan.....	800	810
Arnel.....	760	775
Darvan.....	825	850
Fortisan.....	775	785
Dynel.....	815	820
Dacron.....	800	810
nylon.....	845	855
nylon-6.....	785	800
Orlon.....	785	800
silk.....	835	840
Verel.....	835	840
Vicara.....	800	810
vicuña.....	850	855
Vinyon-HH.....	795	805
viscose.....	765	775
Zefran.....	760	775

ing, and (2) melting and bead formation prior to decomposition. A broad spectrum of thermal stability was obtained from the various fiber types. The data indicate that at elevated temperatures Dynel, silk, Verel, and Vinyon-HH are the least flammable. The most stable of the fiber types at temperatures above 800° F. are Dynel, Orlon, Verel, and vicuña. Therefore, based on the test methods used, Verel and Dynel are the most stable and least flammable of the fiber types investigated.

The same properties were studied for 50/50 blends of these fibers with cotton and for a series of nylon-cotton blends of varying proportions. The effect of blending is to change the melting, flammability, and thermal stability of a fiber system. The undesirable bead formation of the synthetic fiber at high temperatures is eliminated by the addition of a small amount of cotton. Differences between experimental and calculated results were observed and probably can be attributed to chemical interactions at elevated temperatures of the decomposition products of one component of the blend with the other component.



## FABRICS AND COATINGS

*Introduction*

The literature relating to the thermal degradation of elastomers and fiber-forming polymers is extensive.<sup>15-22</sup> However, a critical study of the interactions of fabrics composed of natural, regenerated, derivative, and synthetic fibers of different chemical composition and compatible textile coatings at elevated temperatures has not been reported.

In this study the fabrics used were of 3 fiber types: cotton (cellulosic) representing a natural type, nylon (polyamide), and Orlon (acrylic) representing the synthetic types. A glass fabric was used for control purposes. The fabrics were of similar weave and construction (plain weave—3.0 to 4.5 oz./sq. yd.). The 3 elastomers were butyl rubber (an isobutylene diolefin copolymer), Hypalon 20 (a methacrylic acid polymer) and Neoprene W (a polychloroprene). These coatings were commercially available, and were provided free of additives and pigments except for small amounts of necessary curatives and stabilizers.

*Experimental*

Idealized coated-fabric systems of definite composition were prepared on a laboratory-size spreader. The fabric was held under tension in the clamps of the apparatus, and the elastomer in a benzene solution containing approximately 20 per cent solids was applied with a movable blade. The coated fabrics were dried under a bank of infrared bulbs to evaporate off the solvent, then air-dried for 24 hours, and cured in a circulating-air oven at a temperature of 300° F. for 30 min. The fabrics were coated on either one or both sides to contain approximately 50 per cent fabric and 50 per cent elastomer (TABLE 9).

As a specimen holder, 5-mil aluminum sheeting was cut into a 6 × 3-inch section and folded at an angle of 60°. A 2 × 2-inch sample of fabric was stapled to the aluminum at the open end in such a way as to hang free of the aluminum backing. Samples coated with elastomer on one side only were all positioned on the holder, coated side out. The temperatures selected for pyrolysis (based on statistical considerations for the analysis of the data) were: 502, 589, 675, 761, and 846° F. The time of pyrolysis was 2 min., and was recorded from the instant the door of the furnace was opened to place the sample in its interior. Immediately upon its removal, each sample was quenched in a desiccator filled with carbon dioxide to prevent additional degradation due to afterglow and afterflame. Duplicate samples were pyrolyzed in an order randomized with regard to sequence of temperature, fabric and coating type, and replication. Thermal response (measured by loss in weight and temperature change during pyrolysis), melting characteristics, and flammability (measured by minimum temperature for ignition) were used to determine the high temperature characteristics of the untreated substrates, of the coatings (applied to glass), and of the coated fabric systems.

*Data and Results*

*Loss-in-weight data.* Curves of thermal behavior (loss-in-weight as a function of temperature) were constructed from plots of differences in sample weight before and after pyrolysis. The data upon which these curves are based are

averages of two replicates at each of the five temperatures. The errors estimated as 95 per cent confidence limits of the means are: cotton systems 5 per cent, Orlon systems 3 per cent, and nylon systems 8 per cent (at the two higher temperatures).

The loss-in-weight data for the fabrics and coatings are plotted in FIGURES 8 and 9. The loss-in-weight data for the coated-fabric systems are plotted in FIGURE 10 (coated cotton), in FIGURE 11 (coated nylon), and in FIGURE 12 (coated Orlon). Hypothetical decomposition curves for each fabric-coating system are also given. These curves were obtained by plotting the values obtained by the weighted addition of the observed decomposition value for 100

TABLE 9  
DESCRIPTION OF COATED-FABRIC SYSTEMS

Fabric type	Coating type	Coating method	Code	Coating/fabric ratio
Cotton	Butyl	single	CBS	48/52
		double	CBD	49/51
	Hypalon	single	CHS	49/51
		double	CHD	50/50
	Neoprene	single	CNS	49/51
		double	CND	50/50
Nylon	Butyl	single	NBS	53/47
		double	NBD	54/46
	Hypalon	single	NHS	50/50
		double	NHD	53/47
	Neoprene	single	NNS	51/49
		double	NND	52/48
Orlon	Butyl	single	OBS	49/51
		double	OBD	53/47
	Hypalon	single	OHS	49/51
		double	OHD	48/52
	Neoprene	single	ONS	51/49
		double	OND	52/48
Glass	Butyl	single	GBS	53/46
		double	GBD	50/50
	Hypalon	single	GHS	55/45
		double	GHD	51/49
	Neoprene	single	GNS	49/51
		double	GND	49/51

per cent substrate and 100 per cent coating (as applied to glass) at each of the five temperatures.

The loss-in-weight data of the fabrics, coatings, and the coated-fabric systems were evaluated for significant interaction effects by testing against error in replication (or an estimate thereof), using the statistical technique of analysis of variance. This analysis may be summarized as follows: the thermal stability of the coated-fabric systems is influenced by the type of fabric and the type of coating in the system. The method of application of the coating, to either one or both sides of the fabric, was not significant in its effect on loss in weight. The two-factor interactions,  $T \times C$  and  $T \times F$  (temperature by coating type and temperature by fabric type), were significant on the weight losses of the coatings, of the fabrics, and of all coated-fabric systems, except those of nylon.

*Flammability.* With regard to flammability, as measured by the temperature at which the materials first ignited, the data indicate that, for the coatings applied to glass, butyl was more flammable than either Neoprene or Hypalon;

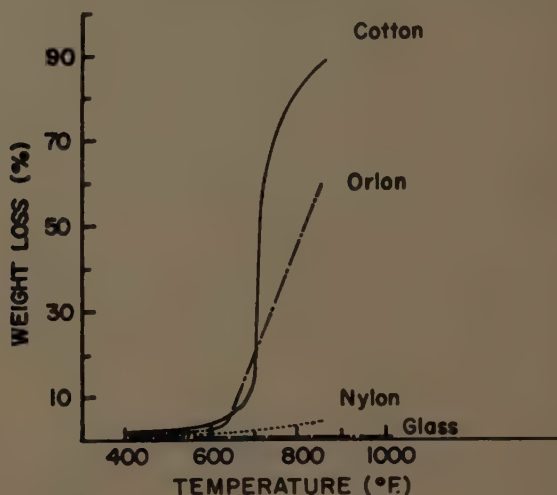


FIGURE 8. Thermal stability of fabric types.

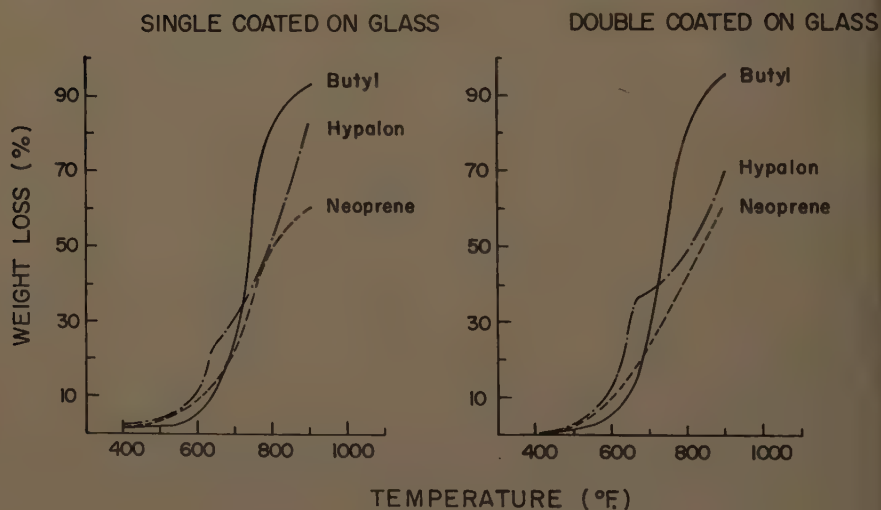


FIGURE 9. Thermal stability of coating types.

for the fabrics, cotton was more flammable than nylon or Orlon. Butyl-coated Orlon was more flammable than the other coated Orlon samples. All coating types increased the flammability of nylon to about the same extent. The butyl coating increased the flammability of the cotton. The flammability of the other coated-cotton systems was approximately the same as that of the untreated base fabric.

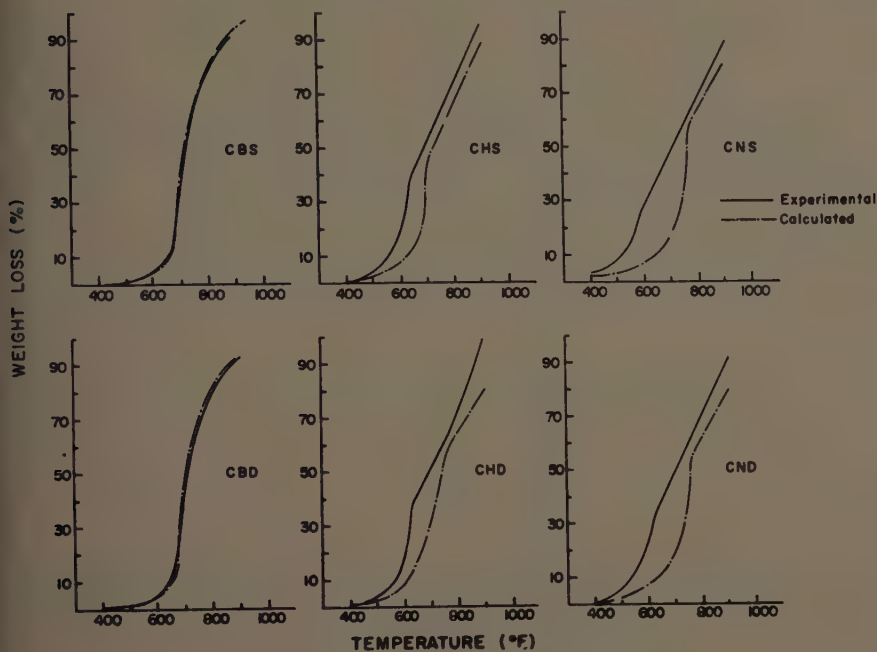


FIGURE 10. Thermal stability of coated cotton.

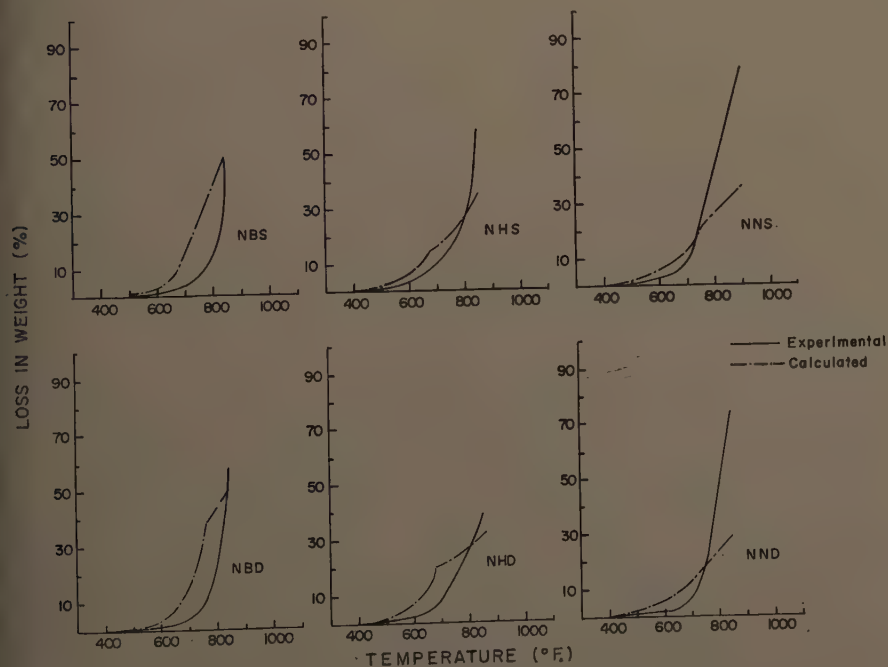


FIGURE 11. Thermal stability of coated nylon.

*Differential thermal data.* The highest and lowest temperatures reached during the pyrolysis of each sample at an initial oven temperature of 675°, 761°, and 846° F. were recorded (TABLE 10). Under the experimental conditions no temperature change would be noted if a thermally inert material were present instead of the test samples. The differences between the extreme temperatures and the starting temperatures are listed in TABLE 10. A positive sign for the difference indicates an exothermic reaction, a negative sign an endothermic reaction. Although basically the thermal decomposition of cotton is endothermic, its decomposition under the conditions of test was exothermic; the de-

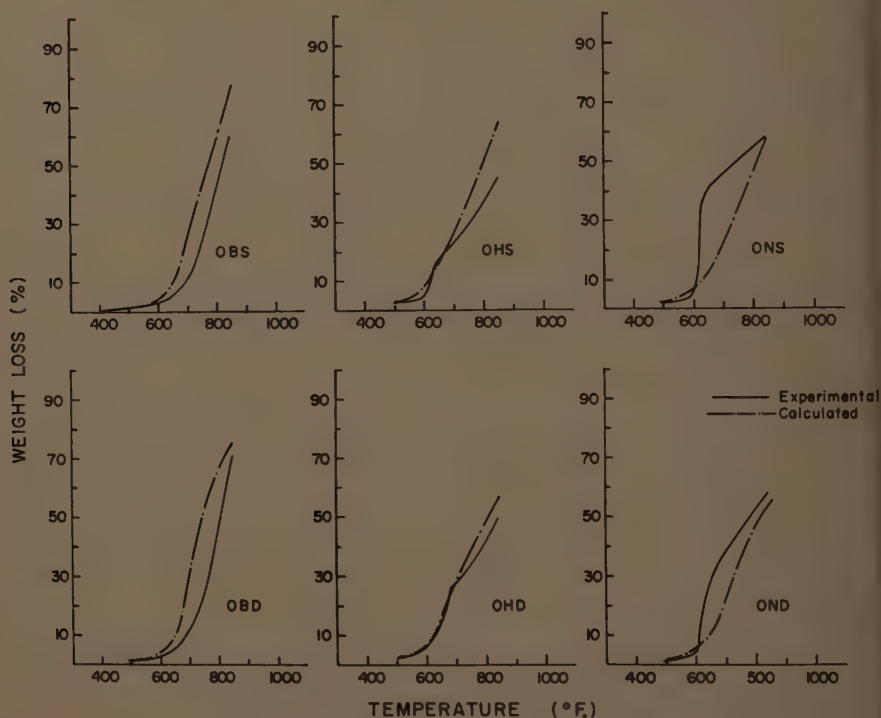


FIGURE 12. Thermal stability of coated Orlon.

composition of nylon and Orlon was endothermic within the temperature range studied. These data can be correlated with the "melting" behavior of cotton, nylon, and Orlon (see under FIBERS AND THEIR BLENDS). The melting prior to decomposition of nylon and Orlon is an endothermic physical phenomenon; this reaction predominates at the lower temperatures. Some minor exothermic decomposition reactions may also occur simultaneously. Cotton became charred without prior melting.

The decomposition of the butyl coating was highly exothermic, whereas that of Hypalon and Neoprene was slightly exothermic. In general, the decomposition of the coated-cotton systems was exothermic. The decomposition of the coated-nylon fabrics was endothermic at first, but became exothermic at higher temperatures, although not to the same degree as the coated-cotton systems.



The coated Orlon fabrics were slightly exothermic in their decomposition, except in the case of the butyl-coated samples, where the decomposition was highly exothermic. These data may be correlated with flammability data. Generally, the more exothermic the reactions of thermal decomposition, the lower the temperature at which flaming was first noted.

The difference between the experimentally obtained temperature for the decomposition of a coated fabric and that calculated from the behavior of its individual components (at initial temperatures 675, 761, 846° F. [TABLE 11]) may be used as an index of either chemical interactions of the products of the decomposition of the coating on the decomposition of the substrate or of the

TABLE 10  
DIFFERENCES BETWEEN STARTING TEMPERATURES AND TEMPERATURES  
REACHED DURING PYROLYSIS

	Cotton	Nylon	Orlon	
Starting temperature 675° F.				
	0	-8	-4	
Butyl.....	0	-8	0	0
Hypalon.....	13	-4	5	18
Neoprene.....	13	-4	9	8
Starting temperature 761° F.				
	17	-17	-13	
Butyl.....	85	0	-5	182
Hypalon.....	13	-5	4	4
Neoprene.....	17	0	4	-14
Starting temperature 846° F.				
	55	-13	-9	
Butyl.....	59	51	55	108
Hypalon.....	42	25	0	16
Neoprene.....	51	46	4	8

physical effects of the coating on the substrate (such as melting and absorption). In this case a positive sign indicates that the experimentally obtained value is more exothermic than the calculated value; a negative sign indicates that the experimental value is more endothermic.

*Stability of fabric structures.* Uncoated cotton fabrics retain their structure even when pyrolyzed at the higher temperatures, whereas the uncoated-nylon and -Orlon fabrics melted into beads at the lower temperatures. Data relating to this stability behavior were evaluated using the following rating scale: (1) behavior of coated fabric system better than base fabric with regard to over-all retention of physical structure; (2) equal in performance to the base fabric; and (3) poorer in performance than the base fabric, and are shown in TABLE 12. In general, coatings helped the nylon and Orlon retain their fabric structures. The nylon samples coated with butyl and Hypalon melted into beads at all temperatures within the range studied. In contrast, the Neoprene-coated samples partially retained their initial fabric structure after heating. In the case

TABLE 11

DIFFERENCE BETWEEN EXPERIMENTAL AND CALCULATED TEMPERATURE  
DIFFERENTIALS AT VARIOUS STARTING TEMPERATURES

Coating type	Temperature differentials at initial temperature		
	675° F.	761° F.	846° F.
Coated-cotton systems			
Butyl.....	0	-15	-23
Hypalon.....	4	3	6
Neoprene.....	9	15	19
Coated-nylon systems			
Butyl.....	-4	-82	3
Hypalon.....	-9	1	23
Neoprene.....	-4	16	48
Coated-Orlon systems			
Butyl.....	2	89	5
Hypalon.....	-2	8	-4
Neoprene.....	7	18	4

TABLE 12

COMPARISON OF THE BEHAVIOR OF THE COATED FABRICS  
WITH THAT OF THEIR BASE FABRICS

Temperature	Butyl	Hypalon	Neoprene
Coated-cotton systems			
(°F.)			
502	2	2	3
589	2	3	3
675	2	3	3
761	3	1	1
846	3	1	1
Coated-nylon systems			
502	2	2	2
589	2	2	1
675	2	2	1
761	2	2	1
846	2	2	1
Coated-Orlon systems			
502	2	2	2
589	2	2	2
675	3	2	2
761	3	1	1
846	3	1	1

of the Orlon fabrics, some improvement in stability of the base fabric was noted with the use of Hypalon and Neoprene as coatings at temperatures above 761° F. Below this temperature, coatings, in general, detract from the inherent structural stability of cotton. At more elevated temperatures the Hypalon- and Neoprene-coated cottons showed a better retention of structure than the untreated control.

### Conclusions

Significant differences were found in the thermal stability, flammability, and melting characteristics of the fabrics and of the coatings, and among the various fabric-coating combinations. Marked departures were apparent in these characteristics of a coated-fabric system from those which could be predicted from the behavior of its components.

Differences were noted in the energy values associated with the decomposition of the fabrics, of the coatings, and of the fabric-coating combinations. In part these can be related to the melting characteristics and flammability of these materials. In addition, the experimental temperatures for the decomposition of the coated-fabric systems differed from those calculated from the behavior of their components.

### Acknowledgment

The contribution of J. C. Whitwell in the design and analysis of the statistical program, and the assistance in the laboratory of Edward B. Jeffries, Alfreda Bruen, and Sandra Glassman are acknowledged.

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# HIGH-TEMPERATURE CHARACTERISTICS OF INORGANIC FIBERS

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It was Alexandre Dumas the elder who, in his famous *The Count of Monte Cristo*, wrote: "Great is Truth. Fire cannot burn . . . it." Flimsy as an abstract shroud of truth may seem as a protective barrier against the depredations of high temperature and fire, it must be admitted that Dumas had a point; for where but in the truth of scientific fact can man seek the knowledge needed to overcome the huge obstacle that fire or high temperature presents to his determined march toward the ultimate truth?

Since primitive days man, when faced with problems of extreme high temperatures, has almost instinctively sought his answers in mineral or inorganic materials. Today, with ever-expanding modern technologies relentlessly demanding better and better performance of textile structures at higher and higher temperatures, he finds himself suddenly plunged into the frenetic task of gathering up all known data on inorganic fibers. From this he hopes to draw some basis from which he may be able to engineer the specific textile structures or composites that are so urgently required.

It is here that man encounters his first frustration, for he is confronted with the terrible realization that, old as his knowledge of inorganic fibers may be, the type of information he now seeks is of a newer type than that gathered by his counterpart of a generation ago. Thus the table of data he has been hoping for contains altogether too many blank spaces, and even Dumas would be forced to concede that today's fire would readily lick through this sparse veil of truth.

The need is for real basic exploration, for a clearer understanding of the physical and chemical properties of these inorganic fibers, not only at elevated temperatures, but at elevated temperatures under specific environmental conditions and as part of very complex systems and structures, the high-temperature characteristics of whose individual elements must thoroughly be understood before intricate interrelationships can be established.

It is the aim of this brief survey to point out a few instances of some fine work that has already been done in this basic research and measurement area, and it is also intended that from these few illustrations the need for more and more work in such areas may be reflected. This paper may be regarded as a plea. Let there be no mistake about it, this type of work is an important element in the next step in man's forward march. The asbestos wick the Greeks and Romans ignited as an offering to their gods is no longer adequate, for today man is preparing himself to storm the very chariot of Apollo.

Asbestos fiber, indeed, has been with us since very ancient times, and its use in those areas where fire, heat, and acid resistance as well as good durability are needed is well known. However, even in this old familiar fiber, the need to know it better is recognized and, during the past few years it too, is coming under the closer scrutiny that characterizes the study of some of the newer synthetic inorganic fibers. At the Asbestos Textile Institute, Philadelphia,

Pa., some very meaningful work is now going on, and M. C. Shaw, who himself has done some excellent work in this field, has been kind enough to supply me with some of the information he has been gathering.

Asbestos, of course, is of several varieties, but the chrysotile type, because of its superiority in textile processing and its good heat resistance, accounts for 95 per cent of the total world production of natural mineral fibers.<sup>1</sup> The chrysotile fiber is the most flexible asbestos fiber.<sup>2</sup> TABLE 1 shows a comparison of its tensile strength with that of other fibers.<sup>3</sup> It should be noted that the average of 56 chrysotile fibers tested in this study was 72,000 psi.

TABLE 1  
COMPARISON OF TENSILE STRENGTHS OF VARIOUS FIBERS WITH ASBESTOS\*

Type of fiber	Tensile strength (psi)
Acetate rayon.....	18,000 to 23,000; 22,000 to 30,000†
Nylon.....	65,000 to 80,000; 88,000 to 117,000†
Glass.....	250,000 to 315,000
Orlon.....	60,000 to 80,000
Cotton.....	42,000 to 125,000
Silk.....	45,000 to 83,000
Wool.....	17,000 to 28,000
Asbestos (Chrysotile).....	18,000 to 469,000‡

\* Tests conducted by Harris Research Laboratories, Washington, D.C.

† Depending on type.

‡ The average tensile strength of 56 asbestos fibers tested was 72,000 psi.

TABLE 2  
EFFECT OF HEAT ON TENSILE STRENGTH OF CANADIAN CHRYSOTILE CRUDE\*

	Tensile strength (psi)	Per cent of original tensile strength
Original crude—no heat.....	131,000	—
Heated 3 minutes at 600 F.....	120,000	91.6
Heated 3 minutes at 800 F.....	96,000	73.3
Heated 3 minutes at 1000 F.....	78,000	59.5
Heated 3 minutes at 1200 F.....	42,000	32.0

\* Reproduced by permission of the *Canadian Mining and Metallurgical Bulletin*.<sup>12</sup>

Chrysotile is a hydrated silicate of magnesium. In the research laboratory of the Asbestos Textile Institute, thermal investigations revealed that the chrysotile structure is maintained up to about 1490° F.<sup>2</sup> Above this point it is converted into the nonfibrous crystalline structure, olivine. At 750° F. a marked degradation of fiber quality is noted, and this is due to the permanent loss of some water of crystallization. As the temperature is increased, more and more of this water of crystallization is lost, with accompanying loss of strength. At 1300° F. almost all this water is depleted.<sup>4</sup> TABLE 2 shows the effect of heat on the tensile strength of chrysotile and, in FIGURE 1 a curve shows the rate of the removal of the water of crystallization with increase in temperature.<sup>5</sup>



More of this work aimed at fundamental knowledge of the asbestos fiber itself is currently being pursued at the Asbestos Textile Institute and in the laboratories of the asbestos textile industry, and we shall be hearing more about this in the not-too-distant future. Myril C. Shaw of the Asbestos Textile Institute has made available the results of an industry-wide evaluation of asbestos textiles. These fabrics are graded by the industry according to the amount of organic fiber blended with the asbestos, the Commercial Grade containing 75 to 80 per cent Asbestos, the Underwriters Grade 80 to 85 per cent, and the A grades going from A to AAAA, which must contain between 99 to 100 per cent. FIGURE 2 illustrates the overlap in percentage of strength retention at given temperatures of some of these grades. To quote from the Institute's paper,<sup>6</sup> "Generally speaking, it can be assumed that those cloths

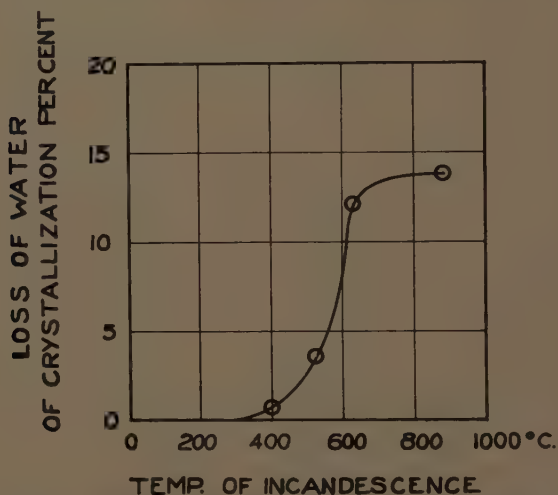


FIGURE 1. Effect of temperature on the loss of water of crystallization of asbestos.

composed of the finer cut yarns will exhibit the highest strength retention characteristics. As a rule, the finer cut yarns contain the greater amounts of high grade or long fiber and this factor contributes to greater initial and subsequent retentive tensile strength properties."

This is a fine illustration of just how important the mechanical engineering aspects of building up a textile structure can become. In his classic Edgar Marburg Lecture, Harold DeWitt Smith stated, "The essence of the textile invention is the building up of large, useful structures . . . by combining countless tiny fibrous units in such ways that the individual strength and toughness of each fiber is accumulated."<sup>7</sup> The main chore of any good textile engineer is to make individual fiber properties additive in the final structure, whether in high-temperature textiles or in the normal textile usages. In the case of the naturally occurring fibers, this problem may always be more difficult than with the man-made synthetics, since fiber-to-fiber uniformity is more controlled in the latter.

The first of the synthetic inorganic fibers I shall discuss is glass. The most common glass fiber is a lime-alumina borosilicate glass that has found wide acceptance as a plastic reinforcement textile, as a fireproof, minimum-care drapery material, and as an electric insulating fiber; here we see the most closely controlled of inorganic fibers. Textile structures of phenomenal strengths have already been achieved on a broad commercial basis, but if a more complete realization of Smith's dream of cumulative or additive properties of the individual fibers could be accomplished, the results would seem miraculous indeed. I can assure you that such work is under way. That it will lead to structures of better service in the high-temperature field is another certainty.

To return to the basic characteristics of the glass fiber at elevated temperatures: I borrow from W. H. Otto's report on work done at the Basic Research Laboratories of the Owens-Corning Fiberglas Corporation, which he has entitled "Mechanical Properties of E-Glass Fibers at Elevated Temperatures."<sup>8a, b</sup> In FIGURE 3, it is seen that the tensile strength of E-glass fibers decreases with temperature from 475,000 psi at room temperature to 175,000 psi at 1200° F. Fibers remained at these temperatures for about 2 min.

In another study of Otto's it is pointed out that when glass fibers are heated they undergo a compaction, an actual contracting in fiber length, and a densification of the fiber accompanied by an increase in Young's modulus. FIGURE 4 illustrates the lineal contraction in centimeters for fibers held at 300, 400, and 500° F. for varying lengths of time.

There is evidence that this compaction or tightening of the glass structure leads to increased high-temperature strength in glass fibers after heat treatment. In FIGURE 5 tensile strength is plotted as a function of the length of heat soak at the testing temperature. It is seen that most of the increase in strength is achieved during the first hour of heat treatment. For treatments of more than 1 hour, the gain in strength due to thermal compaction is more than offset by a loss due to surface weaknesses that develop.

To realize the practical significance of this, compare in FIGURE 6 the strength of an untreated fiber at varying temperatures with the strength of a fiber previously heat-treated at 932° F. and tested at these same temperatures. It should be noted that, when tested at room temperature, the heat-treated fiber has a tensile strength 55 per cent lower than that of the untreated fiber. However, at a testing temperature of 932° F. the heat-treated fiber exhibits 18 per cent more strength than the untreated one.

I lack space in this brief survey to go further into the numerous research programs now under way aimed at a better understanding of the high-temperature characteristics of glass fibers. The few I have cited will give an idea of just how very basic and fundamental these studies must become to provide the knowledge needed to engineer high temperature structures properly. Much of this work, of course, is leading to the development of new glass formulations, and glasses incorporating specialized materials are under study and seem to hold much promise.

Perhaps it would not be wise to leave the area of glass fibers without a quick

glimpse at how a finished textile composed of such fibers behaves at high temperatures. In FIGURE 7 I follow the thermal histories of four 10-mil tapes: a 100 per cent continuous-filament glass tape, a tape woven of a spun or staple glass yarn, a combination glass-asbestos tape, and an all-asbestos tape. As

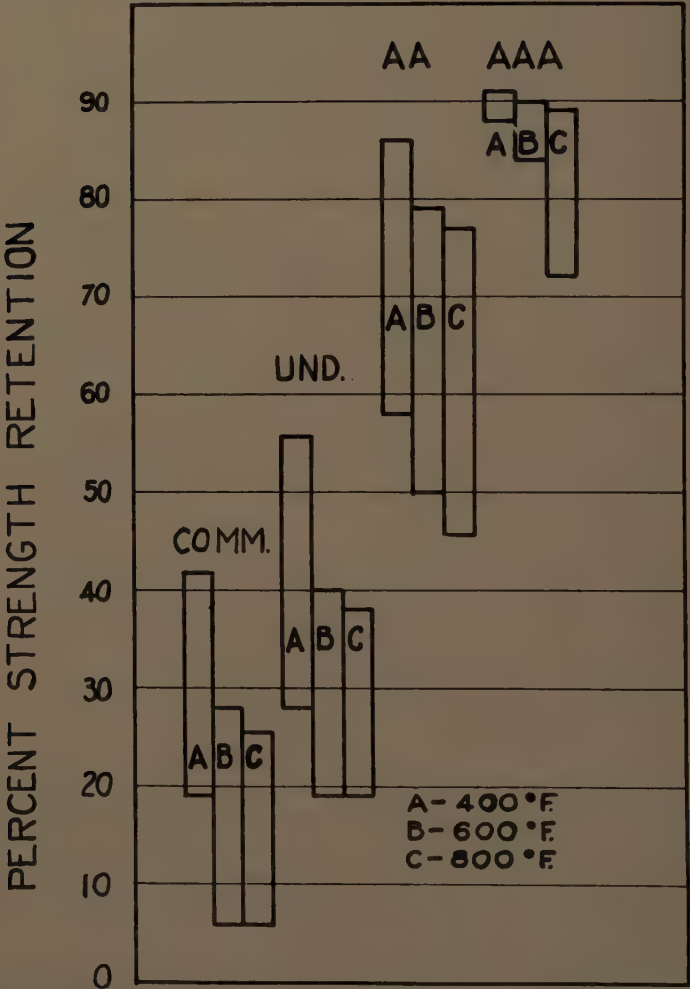


FIGURE 2. Strength retention of asbestos fabrics at various temperatures.

specified, each tape has been exposed to temperatures from room temperature to 1000° F. for 1 hour at each temperature before being tested at 70° F. The superiority of a continuous filament-type fabric with its great tensile strength is at once evident. The staple-type yarns that are so dependent upon inter-fiber friction for tensile strength are severely handicapped from the outset in usages of the type indicated by this test. For an idea of more prolonged exposures FIGURE 8 depicts a study of an all continuous-filament 5-mil glass

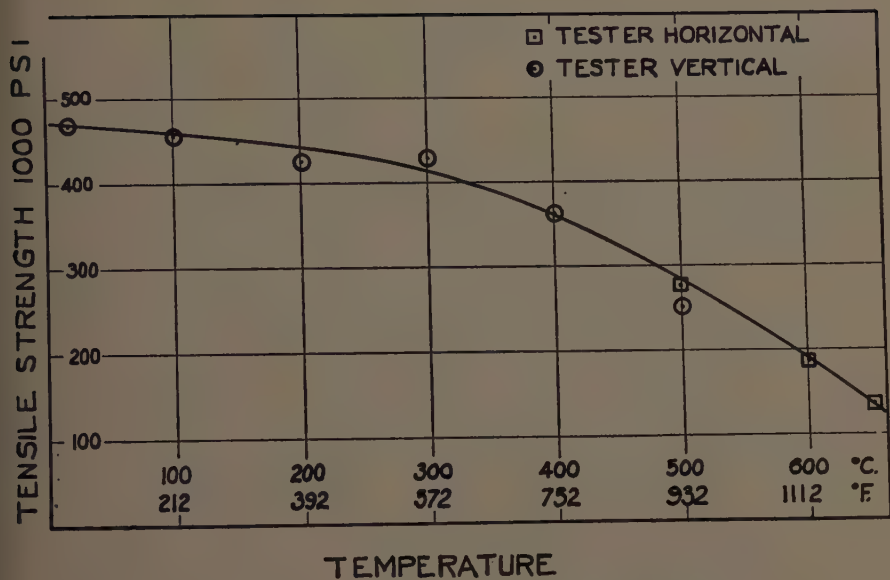


FIGURE 3. Effect of temperature on tensile strengths of glass fibers.

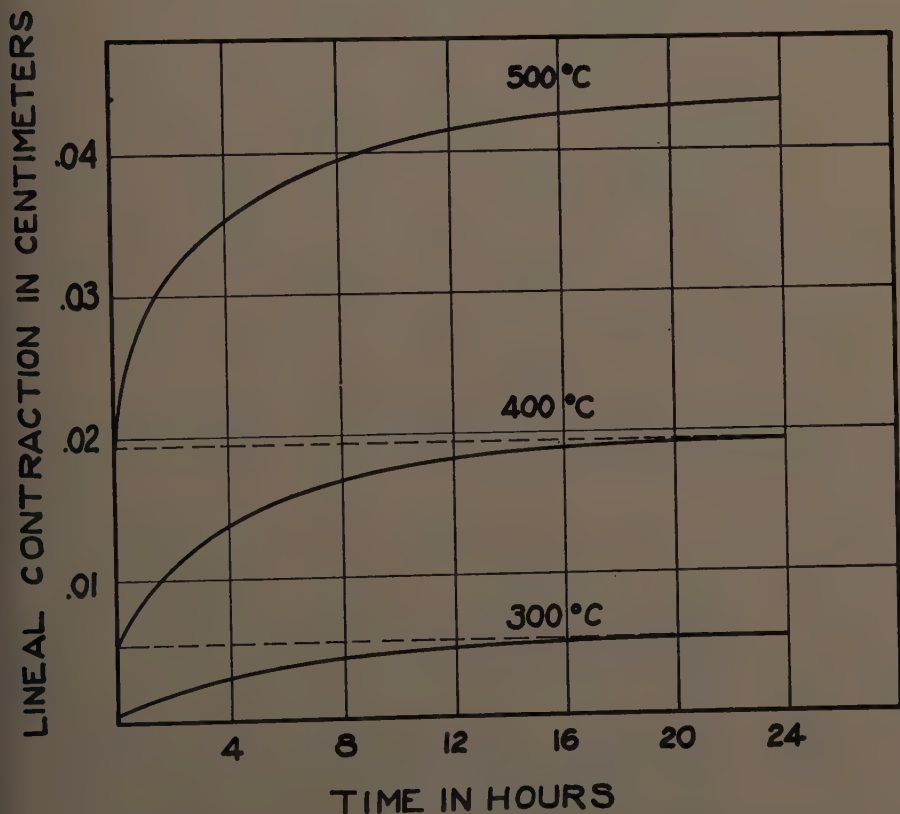


FIGURE 4. Lineal contraction of glass fibers at various temperatures.

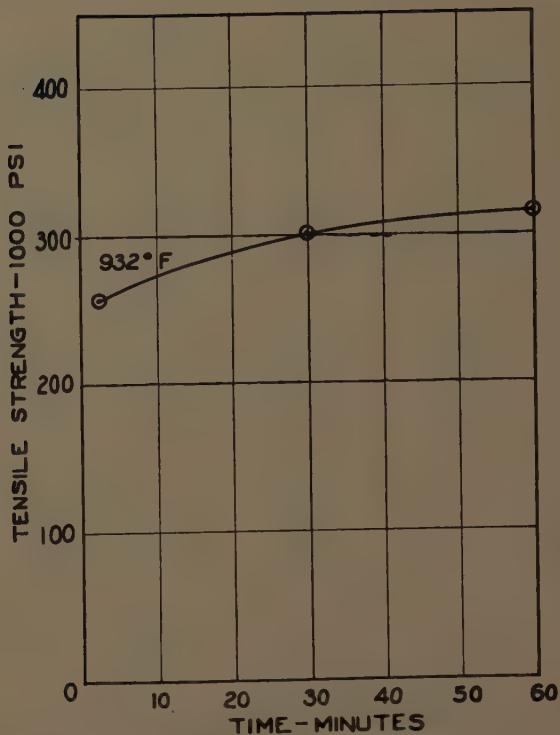


FIGURE 5. Effect of time on the tensile strength of glass fibers at elevated temperature.

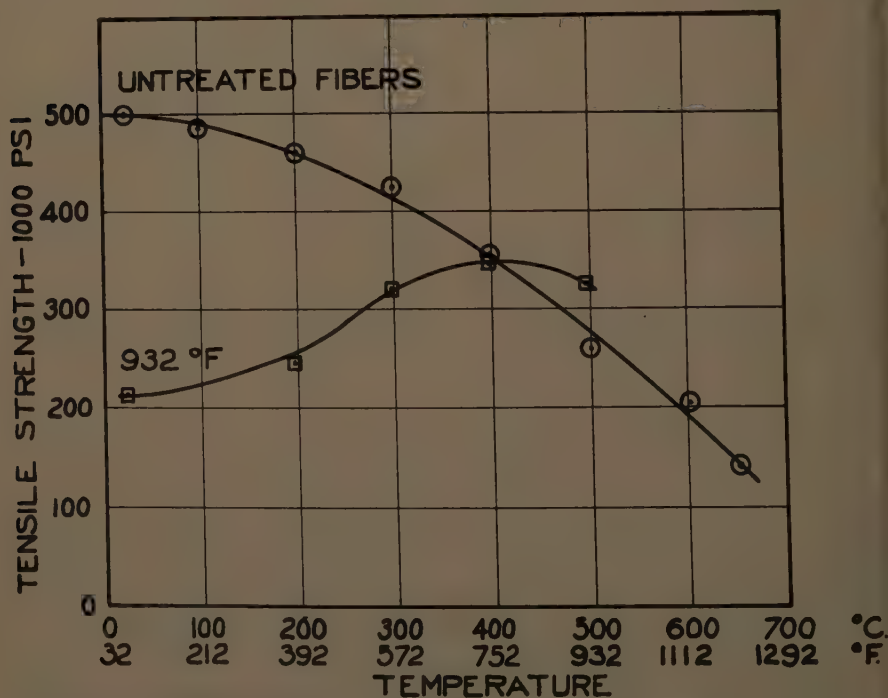


FIGURE 6. Comparison of high-temperature tensile strength of a heat-treated versus untreated glass fiber.



tape subjected to 300° C., 400° C., 500° C., and 600° C. for periods up to 8 hours. You will note that after the sharp initial drop in strength, there seems to be hardly any further weakening; a 25-pound strength 5-mil tape as is evidenced at 600° C. for 8 hours is still a good sound structure.

In going to the next type of high-temperature inorganic fiber, silica, we are not really departing from the type of glass fiber I have just been discussing, for one of the most widely used of this class of fibers is made by the acid leach-

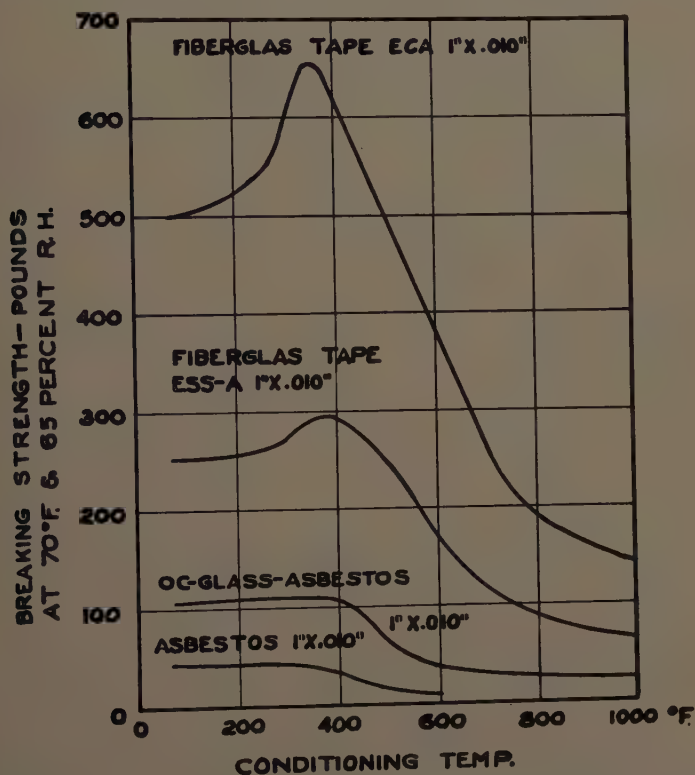


FIGURE 7. Comparison of tensile strengths of glass and asbestos tapes at various temperatures.

ing of glass fibers, resulting in a structure of more than 96 per cent  $\text{SiO}_2$  and, for special uses, up to 99 per cent  $\text{SiO}_2$ . The softening point of these fibers, as would be expected, is above that of normal glass, about 3000° F.; vaporization of the fiber begins at a temperature of 3100° F. Leached glass fiber is said to have very good resistance to thermal shock. It can, for example, be heated to 2000° F. and quickly quenched in cold water without any appreciable change.<sup>10</sup>

Although on a practical basis textile structures of these leached-glass fibers do not exhibit the high-tenacity characteristics of glass yarns and fabrics, braided, woven, and corded structures are in wide use in high-temperature electric insulation applications, in high-temperature reinforced plastics, in thermocouple wire, and in filtration of corrosive materials. If not fired before

use at high temperatures, these fabrics and tapes exhibit a degree of shrinkage. This shrinkage will not occur upon subsequent heatings to the same temperature. An unfired 1-inch tape, 15 mils in thickness and having a breaking strength of about 15 pounds, for example, will shrink just under 15 per cent

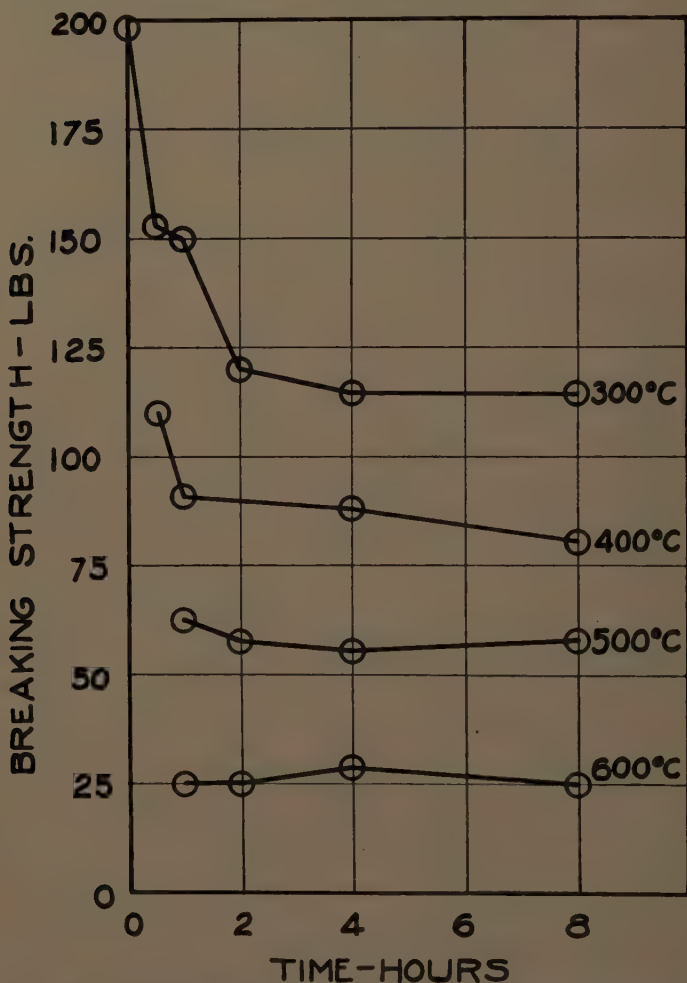


FIGURE 8. Effect of time temperature on the breaking strengths of a 5-mil glass tape.

linearly at 2000° F. This same tape, when fired before exposure to 2000° F., will shrink less than 6 per cent.

It is seen that, in this type of silica fiber, a high-temperature material good for prolonged use at 2000° F. is possible. A property that does need improvement, however, in these leached structures is tensile strength. Much work is now under way to produce leachable glasses with superior strengths and even higher temperature resistance.

There are other approaches to making silica fibers, of course, and one is the drawing of quartz into vitreous silica. In drawing, the quartz structure is changed from the crystalline to the amorphous state. Such work is in the very early stages. No real textile structures have yet been fabricated from such fibers. To quote from a communication from the Bjorksten Research Laboratories dated September 3, 1958: "Silica fibers have been made from quartz of indefinite lengths; i.e., on a continuous production basis, some of which have strengths of 600,000 psi, various batches having average or mean strengths of over 380,000 psi. Such fibers have been made with diameters of from 10 microns to 40 microns. The fibers contain considerable strength at temperatures up to 1000° centigrade. Work is continuing on these."

At the General Electric Company, New York, N. Y., more work in this area is centered about the development of a fused-quartz fiber and this is also

TABLE 3  
TYPICAL BREAKING STRENGTHS OF ALUMINUM-SILICATE TEXTILES (LB.)

Type of textile	Base weight	Normal	After 24 hr. at 1000 F.	At 1500 F.	At 2000 F.
Rope ( $\frac{1}{2}$ in.).....	30 ft./lb. -	80	—	—	—
Rope ( $\frac{1}{4}$ in. with nickel-chromium wire insert).....	46 ft./lb.	300	—	—	—
Cloth (twill weave).....	32 oz./sq. yd.	44	7	6	—
Cloth (plain weave with stainless steel wire insert).....	26 oz./sq. yd.	53	27	25	—
Cloth (double weave with wire insert)...	55 oz./sq. yd.	168	—	97	—
Cloth (twill weave with nickel-chro- mium wire insert).....	40 oz./sq. yd.	117	96	72	52

\* Reproduced by permission from *Materials in Design Engineering*.<sup>13</sup>

in the early stages of development and is being evaluated by several companies and government agencies. At the Monsanto Chemical Company, St. Louis, Mo., a tubular fiber of quartz, three one-thousandths of an inch in diameter is being produced. It is claimed that this tube is so flexible it can be knotted, that is has greater tensile strength than steel, is resistant to high temperatures, and is a nonconductor of electricity.

The final inorganic fiber I shall mention is that of aluminum silicate. Generally, this fiber can be classified in the same high-temperature range as the silica fibers. Such textile products as yarns, ropes, tapes, and woven broad-goods are available in aluminum-silicate fibers. These are made of yarns spun of long-staple fibers; here again tensile strengths of these textile structures is dependent upon interfiber friction and cannot have the high-tenacity properties of a continuous fiber. Organic carriers are sometimes used. Where good tensile strength is needed, glass yarns and metallic wires have been incorporated into the structures.

TABLE 3 supplied by the Carborundum Company, Jersey City, N. J., lists some typical breaking strengths of aluminum-silicate textiles at various temperatures.<sup>11</sup> It will be noted that, in the case of the 32-ounce twill fabric, the initial breaking strength is only 44 pounds. After 24 hours at 1000° F. it still

has 7 pounds left and, at 1500, it is 6 pounds. When a 26-ounce plain-weave fabric with a stainless steel insert is tested, we find that the initial tensile is now 53 pounds, but 24 hours at 1000° F. only reduces this to 27 pounds and, at 1500° F., the fabric still has close to one half of its original strength.

In conclusion, may I point out that, generally, inorganic fibers are not blessed with the property of easy textility that is found in most organic fibers, and that it is in the very attempt to build textile structures of these fibers that a good part of the predicted or predictable properties of the individual fibers themselves is lost. The chore of making fiber properties additive in a textile structure is perhaps simpler with continuous-filament fibers, but even here the textility of an inorganic fiber is dependent upon protective agents and surface treatments. More work certainly is needed here. How wonderful it would be if the one-half million, or the million, or even the two and three million psi that from time to time is spotted in the testing of individual inorganic fibers could be realized in the final textile structure!

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# THE EFFECTS OF VERY HOT GAS ON ORGANIC MATERIALS\*

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One of the problems involved in the development of satellite and long-range missile vehicles is protection from thermal damage during re-entry into the atmosphere. TABLE 1 has been compiled to provide some concept of the severity of the environments to which such vehicles may be exposed. Note that the 5000-mile missile will be exposed to air at temperatures above the melting and vaporization temperatures of any known material. Furthermore, scientists are uniformly pessimistic about the prospects for discovering new materials that will be stable at these temperatures. As a result, the rate at which a material fails can be important. If a substance can be found that erodes slowly enough, it might insure survival of the vehicle until completion of its mission.

Unless one concludes that the entire story is told in TABLE 1, it should be noted that there are a variety of re-entry problems. For example, a weapon vehicle should have a high terminal velocity to make it less susceptible to interception and to provide less opportunity for local conditions to influence the point of impact. On the other hand, a package of scientific instruments is not likely to be intercepted, and a lower terminal velocity would be acceptable. If a manned vehicle is considered, it is important that the deceleration of the vehicle be kept within tolerable limits.

Allen<sup>2</sup> has shown that the ratio of drag to weight can affect profoundly the amount of heating an unpowered vehicle will suffer during re-entry. A high-drag body can be expected to decelerate at relatively high altitudes where the density of the atmosphere is low. Thus, even though the air temperature (which depends almost only on velocity) may be very high, the heat flux to the body may be kept quite low. This is in strong contrast to a low-drag body that will decelerate at lower altitudes and be subject to much more severe heating.

A remarkable result of Allen's calculations is the demonstration that, while the altitude of deceleration is sensitive to drag, the peak value of the deceleration and its duration are essentially independent of drag.

The actual value of the peak deceleration depends on the gradient of the atmospheric density along the flight path. This gradient depends mainly on the angle of flight to the local horizontal. If the path is vertical, the loading on the vehicle may exceed that suffered when an automobile going 60 miles per hour runs into a brick wall. As a result, a manned vehicle must re-enter the atmosphere nearly horizontal. Obviously, if the value of the deceleration is kept low, its duration must be increased. Thus a manned vehicle must tolerate a longer heating period.

This digression about re-entry emphasizes the fact that the enthalpy level behind the shock wave generated in flight, which is determined only by the

\* The work described in this paper was supported by the Air Force Ballistic Missile Division under contract AF04(647)-269, Washington, D. C.



velocity of the body, does not fix the heat-transfer conditions that are also pressure-dependent. Similar considerations are likely to apply to other design problems so that materials evaluation cannot be based on tests that simulate only temperature or heat transfer.

### Testing

The high cost of hardware and the complexity of flight testing justifies the expenditure of considerable effort in the preflight screening of prospective skin materials for re-entry vehicles. Even laboratory scale work can be quite costly because of the difficulty of simulating the relevant environments. In these circumstances a basic understanding of the interactions of very hot air with various materials is extremely important because it would improve the accuracy of extrapolations from accessible laboratory conditions to those anticipated in flight.

In our experiments, some of which are discussed in this report, we have used a number of test facilities, including hot air generators, chemical flames, a

TABLE 1  
VELOCITIES, TEMPERATURES, AND PRESSURES ASSOCIATED  
WITH TYPICAL MISSIONS DURING RE-ENTRY<sup>1</sup>

Mission	Velocity (ft./sec.)	Temperature (°K)*	Pressure (atm.)*
1000-mile flight.....	11,500	3640	1.87
5000-mile flight.....	22,000	7400	7.25
Satellite (300-mi. orbit).....	25,000	8820	9.45

\* Calculated for altitude = 100,000 ft. Note that ambients for this altitude are  $T = 218^\circ \text{K}$ ,  $p = 0.011 \text{ atm}$ .

solar furnace, and a variety of electric arc devices. Thus studies of thermal erosion have been made in gases with widely varying chemistry, temperature, and enthalpy. It should be pointed out here that only the special arc devices are capable of delivering gas hot enough for a sufficient length of time to simulate the re-entry environments.<sup>3</sup>

Among the variables mentioned above, particular attention should be drawn to the question of the enthalpy or heat content of the gas. This is a variable that determines the amount of heat that flows from the gas to the test specimen. It is related to the temperature, but the relationship is different for different gases.<sup>4</sup>

To show this, values of enthalpy have been plotted as function of temperature for argon, carbon dioxide, and water in FIGURE 1. These have been estimated, using some approximations and assuming a total pressure of one atmosphere. The enthalpy in this figure is the amount of energy required to raise a mole of gas, with the initial composition shown, from some low temperature to that shown on the abscissa. This is also the amount of energy released when the gas is cooled. At the steep portions of the curves, the gas molecules are dissociating, so that the composition at the high temperature is different from that of the original gas.

The erosion of a material in argon at a particular high temperature may, therefore, be considerably lower than that of the same material in water or carbon dioxide at the same temperature, even if purely chemical interactions between the material and its environment are ignored. Similarly, the carbon monoxide-nitrogen mixture from a cyanogen-oxygen flame, which is the hottest chemical flame known, need not give more severe erosion than the somewhat

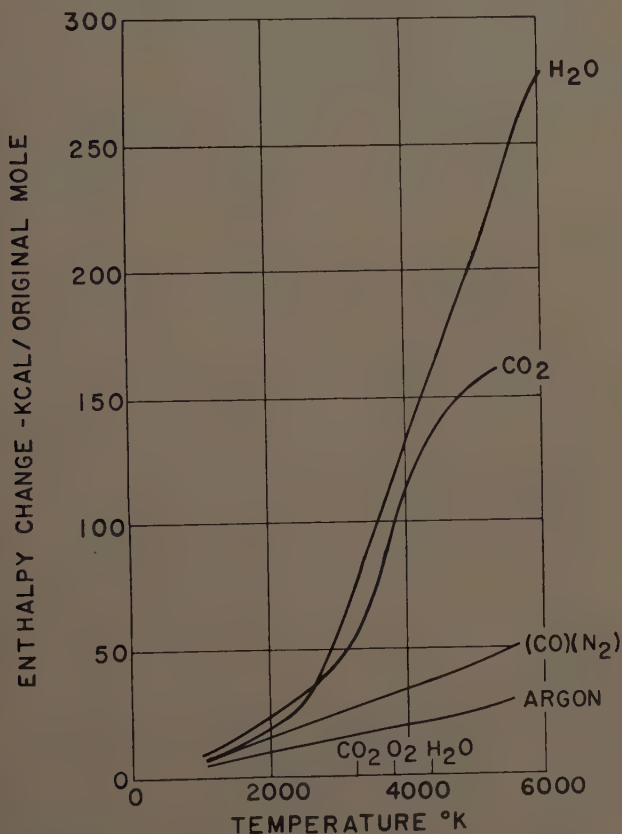


FIGURE 1. Enthalpy as a function of temperature for various gases (approximate).

cooler gases from a hydrocarbon flame that contain carbon dioxide and water. A number of apparent contradictions in test results may be explained when the curves of FIGURE 1 are taken into account.

#### General Results

Several hundred different kinds of metal, ceramic, and plastic materials have been exposed in the different facilities mentioned above. Some of the observations have been summarized in an earlier article.<sup>3</sup> The data shown in TABLE 2 are, however, typical of those obtained in a very hot gas.

A remarkable feature of these data is the special durability of certain organic plastic compositions known to be unstable even below  $400^{\circ}\text{C}$ . Notice that the nylon-phenolic composition is relatively more durable than that of the usual refractory materials, and is exceeded only slightly by that of graphite.

The most obvious explanation of these results is given in terms of the ultimate relative heat-absorbing capacities of these materials.<sup>5</sup> TABLE 3 shows

TABLE 2  
RELATIVE DURABILITY OF MATERIALS EXPOSED TO VERY SEVERE HEATING  
(Ten sec. exposures)

Material	Relative weight loss in water stabilized Arc. ( $7000^{\circ}\text{K}$ . 2000 BTU/ft. <sup>2</sup> /sec.)
Graphite.....	0.81
Nylon phenolic.....	1.2
Silicon carbide.....	1.7 to 6.3
Refrasil*-phenolic.....	2.2
Glass phenolic.....	2.2
Silica.....	2.3
Alumina.....	6.9 to 13.7
Mullite.....	8.22
Zirconia.....	12.9
Copper.....	60

\* H. I. Thompson Co., Los Angeles, Calif.

TABLE 3  
ESTIMATED INTEGRATED SPECIFIC HEATS FROM 300 TO  $5000^{\circ}\text{K}$  AND EQUILIBRIUM  
VOLUME OF GAS GENERATED PER GRAM AT  $5000^{\circ}\text{K}$ . FOR VARIOUS SUBSTANCES

Substance	Heat absorbed, (Cal./g.)	Relative gas volume (gm.)
H <sub>2</sub> gas.....	67,000	1.0
(CH <sub>2</sub> ) <sub>n</sub> organic plastic.....	24,000	0.21
(CH) <sub>n</sub> organic plastic.....	20,600	0.15
C. graphite.....	16,670	0.08
MgO magnesia.....	5,500	0.05
SiO <sub>2</sub> silica.....	2,800	0.05
Cu Copper.....	1,600	0.016
(C <sub>2</sub> F <sub>4</sub> ) <sub>n</sub> Teflon.....	6,300	0.06
H <sub>2</sub> O.....	14,500	0.16
He.....	3,525	0.25

the value of the integrated specific heat for a variety of materials of interest over the temperature interval 300 to  $5000^{\circ}\text{K}$ .

The ultimate relative volume of gas produced by heating each material is also shown in this table. Gas produced by heating can interfere with the convective heat transfer to the body and reduce the effective severity of the exposure.

The data in TABLE 3 have been computed by more or less standard methods assuming that thermal equilibrium will be established at  $5000^{\circ}\text{K}$ . If the material melts or gasifies at a lower temperature, the fluid may be swept off the body before this equilibrium can be established.

In order to allow for this, the integration of the specific heat can be cut off

at the melting or vaporization temperature of the materials. This has been done, and the results are shown in TABLE 4. The ratio of the integral through the fluidization temperature to the integral up to 5000° K. is indicated in the last column.

These calculations provide some basis for understanding the durability of graphite. Notice, however, that no melting points are given for the organic plastics. The reason for this is that the melting point of this type of material does not depend on its gross chemical composition so much as the details of its structure. Phenolic resins, for example, do not melt at all, but are converted to gases of a relatively low molecular weight and to a cokelike residue.

The presence of the coke, which is stable at high temperatures, can reduce the driving gradients at the surface and increase the amount of energy rejected by radiative processes. The results<sup>3</sup> do indeed show that, among organic materials, those containing phenolic resin have outstanding durability.

TABLE 4  
LIQUEFACTION AND VAPORIZATION TEMPERATURES AND ESTIMATED EFFICIENCIES  
OF VARIOUS SUBSTANCES FOR HEAT ABSORPTION

Substance	Melt, °C.	Boil, °C.	Efficiency percentages
H <sub>2</sub> gas.....	-260	-253	0
(CH <sub>2</sub> ) <sub>n</sub> organic plastic.....	—	—	—
(CH) <sub>n</sub> organic plastic.....	—	—	—
C graphite.....	—	4200	99
MgO.....	2800	3350	24
SiO <sub>2</sub> .....	1710	2300	22
Cu.....	1083	2336	6
(C <sub>2</sub> F <sub>4</sub> ) <sub>n</sub> Teflon.....	—	—	—
H <sub>2</sub> O.....	0	100	0
He.....	-272	-269	0

A further test of the rationalizations suggested above is provided by the fact that the high values of the heat absorption of plastics shown in TABLE 2 depend on the existence of high surface temperatures. This is important because, if these are not high enough, the material will not be dissociated to a very great extent and the high calculated values depend largely on the endothermic nature of these dissociation processes.

That this theoretical expectation is realized is shown by the data in TABLE 5. Here conspicuous reversals in the relative rankings of plastic and plastic ceramic compositions occur as the test temperature is changed. These reversals are important also because they emphasize the diversity of practical high-temperature problems.

In TABLE 5 the erosion rate of the most durable material in a particular exposure is assigned the value one. The other materials are then rated according to the ratio of their erosion rates to that of the best. Notice that in gas at 1800° C. glass and Refrasil reinforcements are equivalent and the higher the inorganic content the better the performance. At 3000° C. the higher melting Refrasil provides greater durability. In gas at 7000° C. the difference between glass and Refrasil is lost again. Here, however, the higher the organic content,

the greater the durability. This effect is also noticeable in the 3000° C. gas where, in the resin glass compositions, the lower glass content materials are superior.

### *Discussion and Conclusions*

Actually the behavior of materials exposed to hot gases can be quite complex. We are by no means ready to design the optimum structure for a mission even if we did know the precise enthalpy levels, temperatures, times of exposure, flow conditions, and chemical composition of the environment, as well as the thermal diffusivity and emissivity of the material. The relative importance of these various factors must first be clarified by detailed physical and chemical studies of the nature of the processes that take place under service conditions. The problem is complicated further by the fact that heterogeneous materials, such as reinforced plastics, are involved. Thus, what happens to one phase of the composite may be very different from what happens to another. Some

TABLE 5  
RELATIVE EROSION RATES OF VARIOUS MATERIALS VERSUS TEMPERATURE OF EXPOSURE

Material	Resin percentages	Temperature, °C.		
		1800	2500	7000
Phenolic-glass cloth.....	27	1.0	2.7	2.5
	37	1.2	2.5	2.0
	44	1.6	2.2	2.0
	65	1.7	1.5	1.4
Phenolic-Refrasil cloth*.....	41	1.4	1.0	2.1
Phenolic-nylon cloth.....	57	4.7	2.5	1.0

\* A high-silica fiber produced by H. I. Thompson Co.

discussion of these details has recently been given. It was shown,<sup>6</sup> for example, that under conditions of interest a steady state of damage may be generated. That is, after a short transient, the over-all state of the material remains constant, but the surface recedes at a uniform rate. The thickness of the damaged layer can be quite low. A few millimeters below the exposed surface the temperature rise is so low that even the thermally unstable plastics remain in their original condition.

Our objective here, however, is to point out that, under the most severe conditions of high-temperature service, organic materials that have relatively poor thermal stability may be more durable than refractory metals and ceramics. Some possible rationalizations of this fact are also given that may be useful in the development of even more durable materials and may perhaps help engineers decide what materials should at least be considered for a particular job.

### *Summary*

In this article experiments relating to the behavior of materials at very high temperatures are described. These have been performed in connection with



the problem of protecting satellite and long-rang missile vehicles from thermal damage during re-entry into the atmosphere. It is shown that, under very severe conditions of heating, organic plastics may be more durable than refractory metals or ceramics. Some possible rationalizations of the results are given; these may have some relevance in other aspects of high-temperature technology.

#### *Acknowledgments*

The discussion above is based on a general study of thermal erosion (ablation) in the Aerosciences Laboratory of the General Electric Company. Among my colleagues who have contributed substantially to this study are L. R. McCreight, L. H. Shenker, G. W. Sutton, and S. Scala.

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# RESPONSE OF FIBERS TO INTENSE THERMAL RADIATION

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Elsewhere in this monograph<sup>1</sup> it is pointed out that existing clothing ensembles offer protection to the clothed parts of the body from the thermal effects of atomic weapons to almost the same extent that they provide protection against a cold environment. In other words, a heavy-weight multilayered ensemble can insulate the body from the thermal effects of an atomic weapon, but a light-weight clothing ensemble designed for hot weather wear does not do so.

Another point developed is the fact that clothing ensembles suffer great damage when subjected to the caloric levels of military interest. The damage sustained is sufficiently severe to make it doubtful whether any clothing system, winter or summer, will retain sufficient integrity to ensure limited protection even against the less stressful conditions of the environment. For example, if the wind-resistant qualities of the outer layer of winter clothing are destroyed, the insulating qualities of that ensemble are markedly reduced, and frostbite could become a significant casualty-producer. In summer, destruction of the outer layer of clothing raises the possibilities of sunburn.

When there is added to the foregoing two additional factors, the improbability that complete clothing ensembles may be resupplied rapidly under the new concepts of warfare and the possibility that the soldier may be subjected to multiple exposures from the thermal effects of atomic weapons, it becomes clear that a prime requisite for an outer layer of textile fabric in a military uniform is that it should resist degradation to the extent that the uniform retains the functional properties inherent in its design. In addition, such thermally resistant textile materials should prevent the transmission of energy to the extent that the wearer will not incur burns.

It may be concluded by some, perhaps rightly so, that what is needed and what is actually available are two different objectives, only one of which can be achieved. However, it will be agreed that there should be a method available to catalogue what we have and to provide a standard by which we can measure the potentialities of new materials.

To this end there has been a combined effort on the part of the personnel of the Quartermaster Research and Engineering Command and of the E. I. duPont de Nemours and Company, producers of synthetic fibers, to effect such a technique. The technique is based upon many of the conditions found in the most difficult problem to achieve thermal protection: namely, in hot-weather clothing. In this case, light-weight textile fabrics and dark colors are to be considered under the conditions of military use.

Before discussing the reasons for selecting some of the conditions found within the procedure, it would be best to describe briefly the procedure itself. Three

major components are involved. The first is the irradiating source, the modified carbon arc searchlight. This has been described previously in papers by McQue<sup>2</sup> and Davis.<sup>3</sup> The second component is a representation of the textile material. In this case a nonwoven material is produced from dyed-grey fibers using paper-making techniques. Such are made to represent some of the physical properties found in a 5-oz./sq. yd. cotton poplin. In appearance, the fibrous mat more nearly resembles a blotting paper than it does conventional nonwoven fabrics. Furthermore, it differs markedly from conventional nonwoven materials, for it does not include the large quantity of resinuous binding agents found in such commercial materials.

Finally, there is an assembly designed to position the specimen during its irradiance by the carbon arc. This contains a button type of calorimeter rather than a thermocouple to record the energy transmitted through the test material. Included in the assembly are means to ensure that the test specimen is spaced 0.1 in. away from the calorimeter button.

In addition it is advisable to define at this point some of the conditions of summer clothing design in order that it may be understood later why certain criteria were selected. For example, summer clothing cannot be thought of as a one-, two-, or even a four-layer system at all times. The number of layers varies considerably over the body.

In addition, air spaces are introduced within the garment by folds and as a matter of design to effect comfort. Furthermore, some experimental designs have included the introduction of positive air spaces that enhance thermal protection. Thus air spacing may vary considerably over the body both with respect to location and depth. Fortunately, a location where an air space may not exist is generally one where additional mass is provided by additional layers.

Thus, spacing conditions should be represented. However, selection of the spacing distance of 0.1 in. was predicated upon a technical consideration. At this distance practically all the energy leaving the back surface of the outer layer may be taken into account. One layer of fabric is used to represent the conditions found in the arms and legs. As shown by thermal injury studies, the limbs of the body are highly susceptible to burns.

As previously mentioned, several of the test conditions are based upon considerations of summer-weight clothing. An approach based upon factors of winter clothing was considered but not adopted because of two factors. The first is the limitations of the carbon arc when evaluating such clothing assemblies. In order to effect meaningful differences in such assemblies, the energy required generally exceeds the irradiance capability of the carbon arc; thus relatively long time periods for energy application must be employed, and these are not related to the problem at hand. Second, the properties of fibrous mass as employed for environmental protection in winter clothing behind an outer layer may mask the evaluation of the two properties desired in an outer layer and the ability to resist destruction and to effect energy attenuation. This is particularly true when the outer layer has high conductivity and transmission values.

Before presenting some of the results found in using this method, it is de-

sirable to indicate more completely the technique used for manufacture of the paper mat and the instrumentation employed to measure the energy transmitted through the mats.

In making the mats, initial experiments with several fibers showed that fiber length was important in order to effect reproducibility from sheet to sheet. Furthermore, the effect of crimp found naturally in wool and incorporated in several commercial fibers could be compensated for by using short fibers of one sixteenth-inch length. To obtain uniformity in cutting, the fiber, in the form of top or tow, was fed through a flocking machine and cut to the one sixteenth-inch length.

Single-component mats are made by adding 50 per cent of the total fiber weight to the glass containers of each of two Waring blenders. Each is half filled with water. The slurry is mixed at half speed for 1 to 2 min. to effect dispersion. Two hundred cc. of 0.25 per cent carboxymethyl cellulose is added to each blender and mixing is continued for 10 min. at half speed.

The contents of both blenders are then added to an 8-l. beaker containing 4 l. of water. This is stirred with a Lightning mixer during the addition. Twenty-five cc. of 0.4 per cent Triton X-100, a dispersing agent, and 400 cc. of 0.25 per cent solution of CMC are then added, and mixing is then continued until a good dispersion is obtained. This requires a time period of 10 min. or more. The resultant slurry from the 8-l. beaker is then added to a Noble and Wood paper-making tank and filtered by vacuum to produce a paperlike sheet of fibrous material. Excess water is removed by passing through squeeze rolls, and the samples are oven-dried at 100° C. until constant weight is obtained. After drying, the sheet is approximately 12 in. sq. and in appearance resembles a feltlike material with the fibers randomly dispersed.

It is not my intention to present here all details with respect to the mat-making technique nor, in effect, to present a description or procedure suitable for immediate use by an unskilled operator. Such instruction will be available shortly in report form from the Quartermaster Research and Engineering Center and will include precautionary measures to reduce foam formation, to prevent damage upon removal of the sheet from the Noble and Wood machine, and to compensate for shrinkage.<sup>4</sup>

Control of certain physical characteristics in the resultant sheets is quite important, especially when the sheets are to be used for thermal evaluation of the effect of fiber differences. Furthermore, measurements of the physical properties are necessary to insure evenness within each sheet and between like sheets.

For this purpose the 12-in.-sq. paper mat is weighed and measured. Its weight is controlled within limits of 15.5 to 16.0 gm./sq. ft. This is equivalent to a fabric weight control of 4.9 to 5.1 oz./sq. yd. It is well known that it is very difficult to control woven fabrics within such limits.

Another measurement made is that of thickness. In this case a B.S.I. thickness gauge is used with a pressure of 5.0 gm./sq. cm.<sup>5</sup> However, thickness is not controlled. It is allowed to reach its own dimension, depending upon fiber density. This is not only a simpler approach, but also it did not seem logical to penalize high-bulk fibers and favor low bulk by the use of a fixed thickness. However, it was considered in the method development, which



involved considerable work with cellulosic fibers, and efforts were made to approach the thickness found in a woven poplin fabric of equivalent weight. In cotton mats the thickness was reduced through experimentation, and the resultant mats generally range from two to four times greater in thickness than their comparable tightly woven fabric counterparts.

Three additional measurements are made in order to control reproducibility. These are air permeability, visible light transmittance, and reflectance. Air permeability is determined in accordance with Method No. 5450 of Federal Specification CCC-T-191b.<sup>6</sup> In the case of light transmission the per cent transmission from a 40-watt Mazda lamp is determined. Reflectance for

TABLE 1

UNIFORMITY OF PHYSICAL PROPERTIES ON VARIOUS PORTIONS OF A SHEET  
(SHEET 1, F-1153) OF 50/50 NYLON/COTTON NATURAL COLOR FIBERS

Thickness, B.S.I. 5 gm./cm. <sup>2</sup> (cm.)	0.122, 0.117, 0.129
Weight, (gm./cm. <sup>2</sup> )	0.0169, 0.0168, 0.0167
Apparent density (gm./cm. <sup>3</sup> )	0.1385, 0.1435, 0.1295
Air permeability (cm. <sup>3</sup> /cm. <sup>2</sup> /sec.)	31.4, 30.8, 21.1, 32.1, 31.5
Visible light transmission (%)	1.53, 1.47, 1.50, 1.50
Reflectance against white background (%)	82.0, 81.0, 82.0, 82.0, 81.5
Reflectance against black background (%)	77.5, 78.0, 78.0, 77.5, 78.0
Cover power (%)	93.9, 96.0, 94.7, 93.9, 95.3

TABLE 2

UNIFORMITY OF PHYSICAL PROPERTIES OF NATURAL COLOR NYLON MATS

	Run I		Run II	
	Sheet 1	Sheet 2	Sheet 1	Sheet 2
Thickness, B.S.I. 5 gm./cm. <sup>2</sup> (cm.)	0.132	0.135	0.135	0.130
Weight (gm./cm. <sup>2</sup> )	0.1068	0.0167	0.0167	0.0168
Apparent density (gm./cm. <sup>3</sup> )	0.1262	0.1236	0.1236	0.1292
Air permeability (cm. <sup>3</sup> /cm. <sup>2</sup> /sec.)	70.61	74.73	70.66	77.06
Visible light transmission (%)	2.85	2.97	2.88	2.90
Reflectance against white background (%)	81.5	81.5	83.5	83.6
Reflectance against black background (%)	68.8	68.3	70.0	69.9
Cover power (%)	82.6	81.9	81.8	81.5

control purposes is generally expressed as the "contact-covering power," which is defined as follows:

$$\text{Cover power} = \frac{(R_{wb} - R_{bb}) - RF_{wb} - RF_{bb}}{R_{wb} - R_{bb}}$$

$RF_{wb}$  and  $RF_{bb}$  are the reflectances of the mat against white and black backgrounds, while  $R_{bb}$  and  $R_{wb}$  are the reflectances of the white and black backgrounds.

With sequential sampling techniques each individual paper produced is checked for these properties to ensure uniformity within the sheet. A typical example of the uniformity is shown by the data of TABLE 1.

TABLE 2 presents data illustrating the degree of reproducibility between mats



from the same run, as well as between different runs. It is pointed out that there was an interval of several weeks between each of these runs.

Although the data presented here have been limited to specific instances for illustrative purpose, similar data could be presented for other fibers.

Before proceeding to the evaluation of some fibers using fibrous mats rather than fabrics, it would be best to consider briefly the calorimeter and its mount.



FIGURE 1. Response of fibers to intense thermal radiation. Photo by Quartermaster Corps, United States Army.

Its general appearance is shown in FIGURE 1, and a detailed drawing of its major assembly appears in FIGURE 2.

With FIGURE 2 as a reference, it is to be noted that the sample holder consists of a brass cylinder drilled and tapped on its central axis to receive a 0.324-in. diameter spindle (A). The spindle is drilled to receive the leads from a 30-gauge copper constantan thermocouple soldered to the rear surface of the button calorimeter. Three needles, mounted in the face of the spindle, define the plane occupied by the calorimeter. Contact between the needles and the button is maintained by tension applied to the copper-constantan leads. A brass

ring, 0.1 in. thick with a seven sixteenth-inch-diameter aperture is used to maintain the desired space between the button and the sample (D). In practice, the sample under study is placed into the cap (G), which is then rotated to place the sample in contact with the spacer ring.

As pointed out earlier, it is believed that a comparison of the relative effectiveness of various fibers and fiber blends for hot-weather clothing conditions can be obtained by measuring the thermal energy received at some finite distance (0.1 in.) behind the material.

Accordingly, a copper disc sufficiently thin to measure accurately the energy transferred through or by the mat was fabricated from electrolytic grade copper bar stock. The stock was lathe-turned to approximately three eighths-inch diameter, and discs of approximately 0.014-inch thickness were fabricated. The mass of the disc was determined by weighing with an analytical balance,

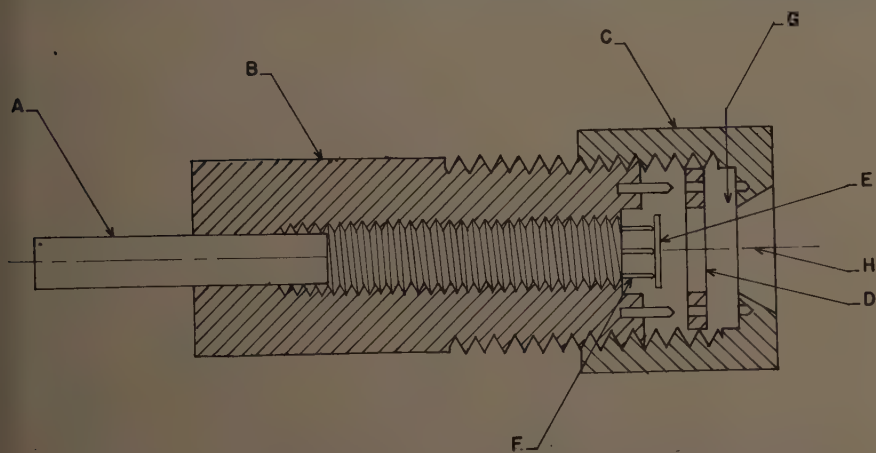


FIGURE 2. Cross-sectional view of calorimeter assembly: (A) threaded spindle; (B) brass cylinder; (C) threaded cap; (D) brass spacer (0.1 in.); (E) calorimeter button; (F) supporting needles; (G) sample location; and (H) aperture.

and thickness was calculated from mass, diameter, and density. The weight of the solder used to affix a 30-gauge copper-constantan thermocouple to the rear surface of the disc was included in the mass of the disc and was assumed to have similar thermal properties. Data used in calibrating the discs will be provided in a subsequent report.<sup>4</sup>

To compare mats with fabrics, initial studies were conducted with mats made from APO-THPC-treated cotton fibers. In this work a comparison was obtained of the energy transferred to the button calorimeter by a woven cotton poplin of equal weight. A detailed description of these two materials is as follows:

**Mats.** This was made in accordance with previously described techniques from undyed cotton fibers treated in silver form to effect an add-on of 16 per cent of the flame-retardant finish THPC-APO.<sup>7</sup>

**Cloth.** This was the standard 5-oz. cotton poplin, Type I, Class A, of MIL-C-342 undyed that had been treated in piece form with THPC and APO to effect an add-on of 20 per cent.

In TABLE 3 are given the weight, thickness, air permeability, and optical properties of each material. Measurements of reflectance and transmittance in the range 0.3 to 0.4  $\mu$  were made with a Beckman Quartz Spectrophotometer and in the range 0.4 to 1.0  $\mu$  with a General Electric Recording Spectrophotometer. Measurements from 1.0 to 3.0  $\mu$  were estimated from data by Ramsley.<sup>8</sup>

TABLE 3

PHYSICAL PROPERTIES OF 5 OZ./YD.<sup>2</sup> COTTON POPLIN (FR) AS COMPARED TO THE MAT

	APO-THPC Matt	APO-THPC Poplin
Thickness (cm.)	0.226	0.0358
Weight (gm./cm. <sup>2</sup> )	0.0180	0.0210
Air permeability (cc./sec./cm. <sup>2</sup> )	58.02	6.67
Reflectance (%)	68.7	67.7
Transmission (%)	11.7	19.7

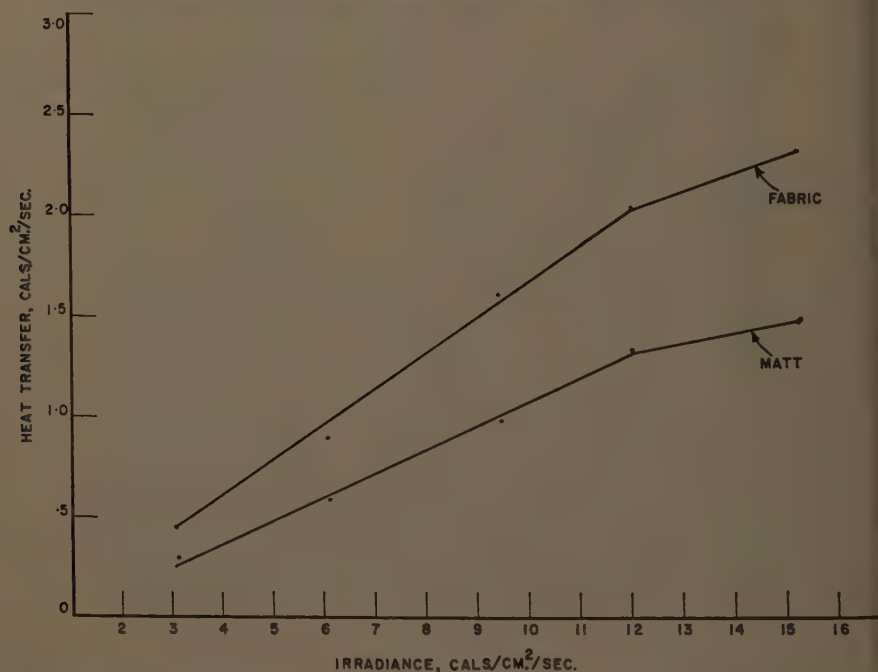


FIGURE 3. Comparison of heat transfer through the fire retardant treated cotton fabric and mat.

The measurements were integrated with respect to the spectral distribution of the carbon arc as reported by Krolak and Davis.<sup>9</sup> The integrated measurements are given in TABLE 3. As shown by the data of TABLE 3, the poplin and mat are equivalent in weight, but differ in thickness. The reflectances are equivalent, but the transmittance differs considerably.

The total heat-transferred data are presented in FIGURE 3. The curves of FIGURE 3 show an excellent agreement between the heat-transfer character-

stics of the woven fabric and the mat. Both curves show a constant increase in heat transfer with irradiance up to 12.1 cal./cm.<sup>2</sup>/sec. At this irradiance both curves indicate that an event occurred that markedly changed the heat-transfer characteristics of the materials. The degree of correlation is further demonstrated by the ratio of heat transferred through the poplin to that transferred through the mat at several irradiancies considered. These data are shown in TABLE 4.

TABLE 4

RELATIONSHIP BETWEEN HEAT TRANSFERRED THROUGH THE WOVEN FABRIC AND THE MAT

Irradiance	Heat transferred through the poplin	Heat transferred through the mat	Ratio poplin/mat
3.1	0.45	0.29	1.51
6.1	0.89	0.58	1.53
9.0	1.45	0.86	1.69
9.5	1.59	0.97	1.64
12.1	2.01	1.30	1.54
15.3	2.28	1.46	1.56

TABLE 5  
HEAT TRANSFER DATA

Irradiance cal./cm. <sup>2</sup> /sec.	Heat transferred during 1.0 sec. pulse cal./cm. <sup>2</sup> /sec.	Total heat, mean cal./cm. <sup>2</sup>	Time for total heat transfer sec. (tp)	Percentage heat transfer occurring during pulse
Poplin				
3.1	0.43	0.45	1.4	96
6.1	0.86	0.89	1.5	97
9.5	1.51	1.59	1.1	95
12.1	1.81	2.01	1.1	90
15.3	2.10	2.29	1.6	92
Mat				
3.1	0.25	0.29	1.4	86
6.1	0.54	0.58	1.4	93
9.5	0.86	0.97	1.2	89
12.1	1.01	1.30	1.7	78
15.3	1.11	1.46	1.6	76

A more detailed analysis of the calorimeter button readings that takes into account time for transfer, reveals in TABLE 5 two interesting observations. First, in the case of both materials, more than 75 per cent of the energy is transferred during the thermal pulse. In the case of the woven-poplin fabric, even though it is a considerably less permeable material than the mat, it has a greater percentage of the heat transferred during the 1.0-sec. period of irradiance.

In addition to possibilities shown for the study of problems of energy transfer, the evaluation of materials in the mat form has shown considerable promise as a method for determining the most suitable fiber blends and individual

fibers. One of the first studies made concerned blends of cotton and nylon. In this case mats were made effecting blends in 10 per cent increments. In FIGURE 4 some of the data extracted from that study are presented.

In this study both the cotton and the nylon fibers were dyed prior to cutting and fabrication into mats. Both were matched to Pearl Grey Cable No. 70,193 of the Standard Card of America, ninth edition.<sup>10</sup> Dyeing was found necessary, rather than pigmentation using carbon black, as has been used previously in fabrics for thermal studies. The reasons for this were twofold.

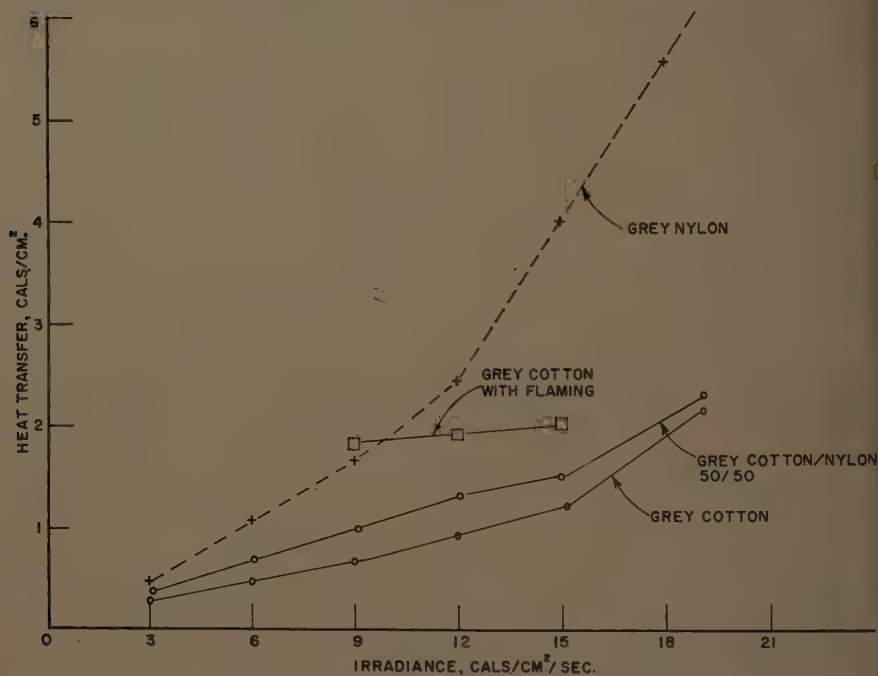


FIGURE 4. Comparison of grey fibers.

(1) When applied using the paper-making technique, carbon black, due to its small particle size, was carried through the mat along with the water when the slurry was dumped.

(2) When sprayed on mat, it often would be quickly removed from the mat surface of some fibers, leaving a highly reflectant surface, thus introducing very uneven test results. This was particularly true of 100 per cent nylon mats.

It will be first noted from FIGURE 4 that there is a marked difference in the behavior of nylon and cotton. However, it must be pointed out that the heat transfer data for cotton were derived from those instances when the cotton did not flame. The blend of 50/50 cotton-nylon approached this data for the cotton. When flaming of the cotton is taken into account, it becomes apparent that the 50/50 blend is superior. Also, this blend did not exhibit afterflame.

Mention should also be made of the fact that at the highest irradiance, 19



cal./cm.<sup>2</sup>, all samples were completely destroyed. Furthermore, all cotton specimens flamed when subjected to 12 cal./cm.<sup>2</sup> and it is for this reason that a point is not shown for that irradiance.

With a blend of cotton and nylon showing better potentialities than either cotton or nylon, the next objective was to find the blend that performed best. Analysis of the mats containing amounts of nylon greater than 50 per cent showed that they performed with decreasing effectiveness as the nylon content increased. Thus, the problem concerned the materials containing the larger amounts of cotton.

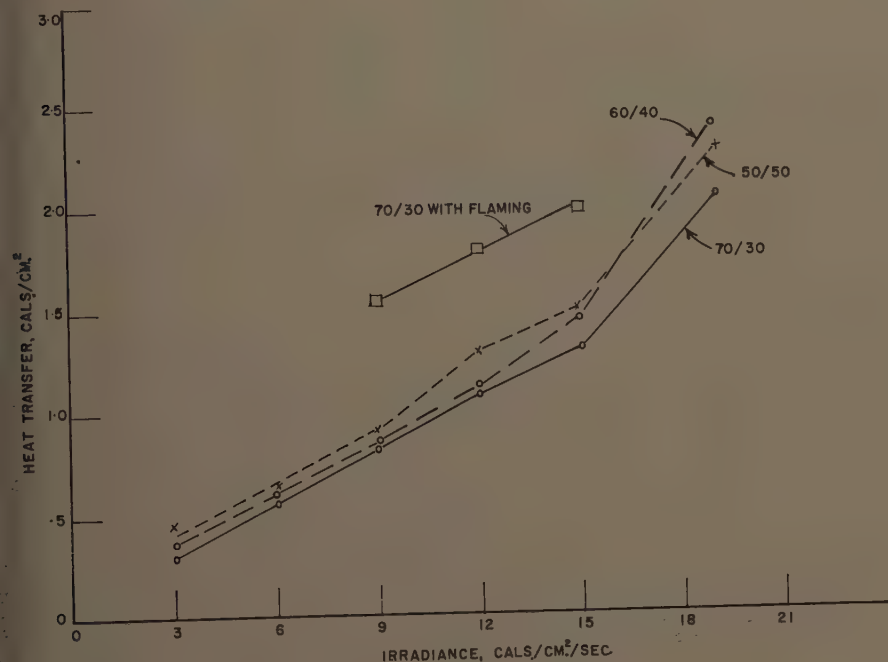


FIGURE 5. Grey cotton-nylon blends.

In FIGURE 5 the data obtained with the 50/50, 60/40, and 70/30 blends are shown. Here, from 3 to 15 cal./sq. cm., the 60/40 blend gave lower heat transmission than the 50/50 blend. On the other hand, the 70/30 blend showed many occurrences of flames.

Fortunately, there existed a series of denim fabrics representing various increments of cotton/nylon blends. A limited amount of this fabric was obtained and evaluated to the extent permitted by the sample size. Here again it will be noted in FIGURE 6 that a blend of 30 to 40 per cent nylon with cotton offers the best promise of effecting the lowest heat transfer.

This information is now being applied in fabric-development studies, and several mills are producing samples.

The method may also be used to evaluate fiber performance. This is illustrated in FIGURE 7. Here are plotted the data obtained with mats of nylon,

wool, the 60/40 cotton blend, and cotton treated for fire resistance, using THPC-APO and applied to both dyed and undyed fibers. The flame-resistant-treated materials are shown as the best performers of this group.

These data also show that desired performance characteristics have not been

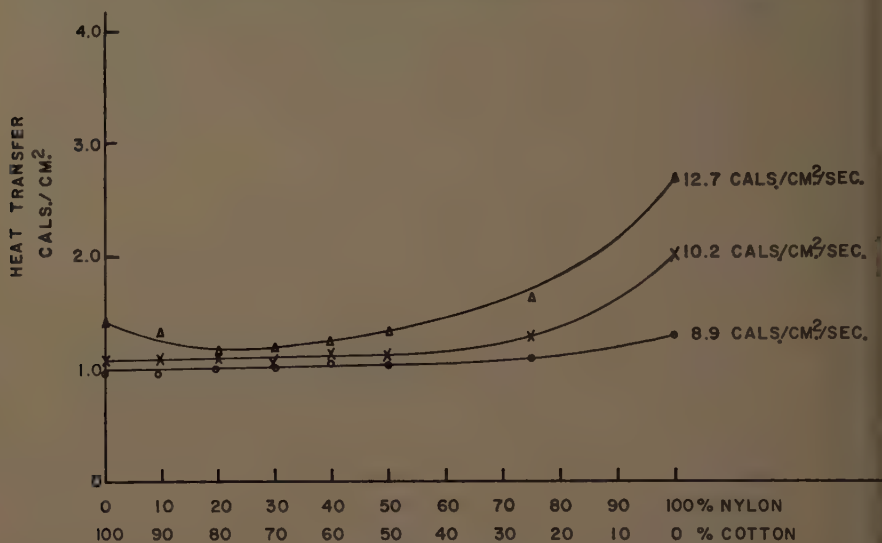


FIGURE 6. Cotton-nylon denims spaced 0.25 in. at 0.5 sec. exposure.

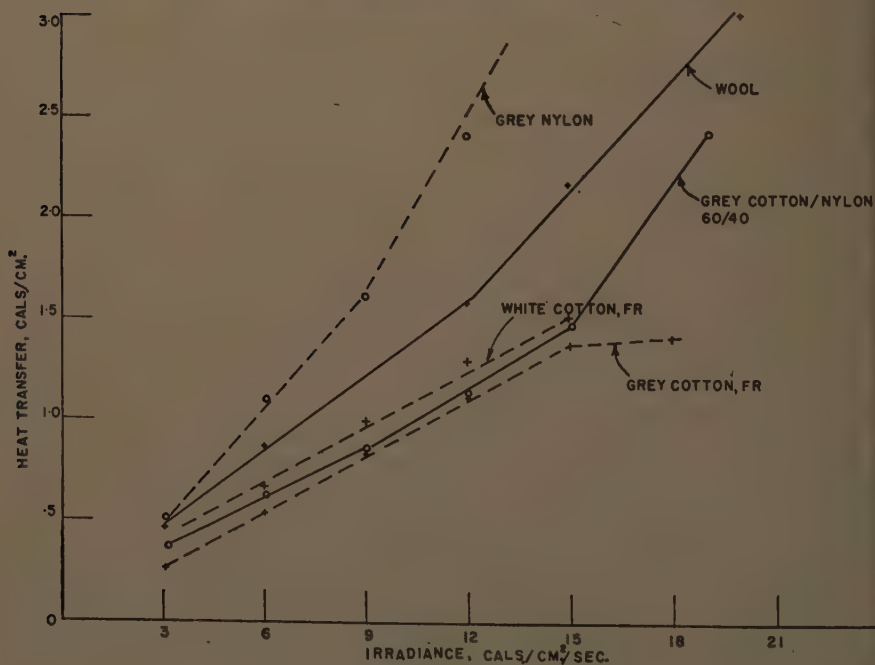


FIGURE 7. Comparison of several materials.

met. There is a long way to go in effecting improvements with respect to energy transmission. Furthermore, all of these materials are functionally unsuitable following exposure to 9 cal./sq. cm.

However, three factors are promising: first, the work that is going on as described in this publication to improve existing fibers;<sup>11</sup> second, the new improved fibers that are constantly being sought by fiber producers to gain a greater share of the commercial market; and, third, the performance shown by the cotton-nylon blends indicating that there may be other blends with even better performance.

A formidable task lies ahead. At present there are available in the Quartermaster Laboratories in Natick approximately 40 sets of papers representing over 450 fabrics. Fiber or fabric producers well know that if these were produced as fabric samples, half a million dollars would be a conservative estimate of their cost. A new arc is being installed to facilitate and expedite their testing.

Aside from the economic features mentioned here, it is felt that the procedure of making the fibrous mats and their subsequent evaluation provides us with a substitute for the woven fabric. Finally the mat provides, through improved control in several of its physical properties, a better material for many studies of a basic nature.

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# EFFECTS OF HIGH-ENERGY RADIATION ON POLYMERS

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Research into the effects of high-energy, ionizing radiation on polymers is receiving increased attention from several points of view: (1) the development of radiation as a tool for basic polymer research; (2) useful modification of polymers by controlled irradiation; and (3) the development of radiation-resistant materials. Of vital importance to all of these areas is an understanding of the basic radiation chemistry that occurs in each specific polymer. Since this monograph is primarily concerned with the thermal and radiation stability of textile polymers, the emphasis in this paper will be on some factors that may influence the effects of radiation on the physical properties of polymers and the possibility of minimizing these effects.

The changes in physical properties of a polymer under ionizing radiation will depend primarily on whether the polymer chains are crosslinked or whether they are degraded. For amorphous elastomers, where complications due to crystalline or "glass" phases are absent, the direction of the radiation effect is reflected in the tensile properties of the material. Crosslinking produces an increase in modulus and a decrease in elongation, while degradation causes decreases in modulus and strength.<sup>1, 2</sup> The primary factor that determines the direction of radiation effect is the chemical structure of the polymer. For example, polyethylene, natural rubber, polydimethylsiloxane (silicone), and nylon are crosslinked while polyisobutylene, butyl rubber, polytetrafluoroethylene (Teflon), and cellulose polymers are degraded.<sup>3, 4</sup> In the particular class of vinyl polymers:



where the main-chain is composed of saturated C-C linkages, it has been shown that crosslinking predominates, but if the tertiary hydrogen is replaced by a methyl group, as in



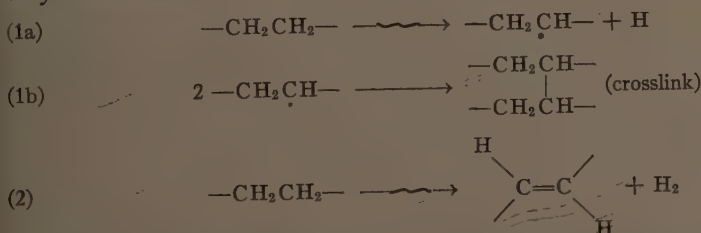
the polymer is degraded.<sup>5</sup> This correlation has been further related to the heats of polymerization and mechanisms of *thermal* degradation for the corresponding polymers.<sup>6</sup>

From the standpoint of radiation resistance, either crosslinking or degradation are undesirable since the former process would lead eventually to a hardening or embrittlement of the polymer and the latter to a softening and loss of strength. Associated with either of these processes are other, often undesirable, chemical effects such as gas evolution. Marked differences in radiation resistance have been recognized for some time, and here again the chemical structure appears to be the determining factor. The early work of Sisman and Bopp<sup>7</sup> showed that cellulose and halogenated polymers, including Teflon, had a

relatively low resistance to radiation, while polystyrene was one of the most resistant polymers tested. The low radiation resistance of Teflon is in contrast to its very high *thermal* stability. The pronounced effect of aromatic (for example, phenyl) groups in increasing the radiation stability of polymers has been well established on a more quantitative basis. Thus, in polyethylene,  $[-CH_2CH_2-]_n$ , about 25 to 30 e.v. of absorbed energy is required to produce a crosslink<sup>8, 9</sup> while in polystyrene,  $[-CH_2CH(C_6H_5)-]_n$ , the energy requirement per crosslink is at least 500 e.v., or about 20 times greater than for polyethylene.<sup>10</sup> Similarly, dimethylsilicones,  $[-OSi(CH_3)_2-]_n$ , require about 30 e.v. per crosslink, but the replacement of about 27 per cent of the methyl groups by phenyl groups raises the value to about 125 e.v.<sup>11</sup> On the basis of physical properties, it has been shown that the useful life of the 27 per cent phenyl-methylsilicone in an ionizing field is 2 to 5 times longer than for the normal dimethylsilicone.<sup>11</sup>

The foregoing discussion has demonstrated the general effect of chemical structure on the radiation stability, cross-linking, and degradation of organic polymers. However, to provide a sound basis for methods of suppressing or minimizing radiation damage, a deeper insight into the radiation chemistry of individual polymers is required.

The radiation chemistry of the polyethylene structure,  $[-CH_2CH_2-]_n$ , has already been examined in some detail, and this polymer may be used as a model to illustrate some factors, other than chemical structure, that should be considered in radiation damage studies. Critical reviews of the radiation chemistry of polyethylene, based on present experimental evidence, have already been published,<sup>12, 13</sup> and only the salient features will be mentioned here. The observed radiation effects in polyethylene can be explained on the basis of two concurrent processes: (1) a free-radical scission of C-H bonds to produce polymer radicals which, under the proper conditions, can combine to form crosslinks; and (2) a nonradical, "molecular" expulsion of  $H_2$  to form a trans-vinylene double bond.



Unlike free-radical polymerizations that are chain reactions and have rates that are strongly dependent on the radiation *intensity* (dose rate), the crosslinking of a polymer such as polyethylene is a nonchain reaction and, in the absence of other competing processes, the crosslinking is apparently not sensitive to the radiation intensity. In the presence of oxygen, however, there is a competition between the crosslinking of the polymer radicals (reaction 1b) and their reaction with oxygen, which suppresses the crosslinking. Thus, in the irradiation of polyethylene in an air or oxygen atmosphere and at low radiation intensities, the diffusion of oxygen into the polymer can alter the radiation



effect from crosslinking to suppression of crosslinking, and even to oxidative degradation. This effect is illustrated by some work of Chapiro<sup>14</sup> who found that for a given grade and thickness of polyethylene, irradiated in air, the dose required to crosslink the polymer to the gel point was  $2.5 \times 10^6$  r (roentgens) at an intensity of 400 r/min. When the intensity was reduced to 100 r/min., degradation, rather than crosslinking, occurred. In a nitrogen atmosphere or in vacuum, the gel point for the same polymer was reached at a dose of only  $1 \times 10^6$  r, and this was now independent of the radiation intensity. The simultaneous effects of sample thickness, oxygen pressure, and radiation intensity in suppressing the crosslinking of polyethylene have been examined in a more quantitative manner by St. Pierre and Dewhurst.<sup>15</sup>

Detailed studies of the effects of additives in the irradiation of polymers have been reported by Turner for natural rubber,<sup>16</sup> by Loughborough and others for several elastomers,<sup>17</sup> and by Prober for polyethylene.<sup>18</sup> Generally, it was found that free-radical inhibitors such as phenols, aromatic amines, and sulfur compounds, added in low concentrations (for example, 1 per cent), retarded the crosslinking, and that in polyethylene about one molecule of inhibitor was consumed in the suppression of each crosslink. Prober showed that in some cases the inhibitor molecule, or its fragments, became chemically bound to the polymer in the inhibition reaction. Moreover, he found that, although the additives retarded the radiation crosslinking in polyethylene, the formation of the transvinylene double bond (reaction 2) was not affected. It may be mentioned, in passing, that these results support the proposal, presented earlier, that the crosslinking and vinylene formation must occur by two independent processes. Prober's results also emphasize a more general problem of protection against radiation damage. Although free-radical processes may be retarded by conventional inhibitors, radiation-induced molecular processes will be more difficult to suppress. An "ideal" protective agent for organic materials is one which, at relatively low concentrations, would very efficiently absorb energy from the substrate and dissipate this energy by nonchemical processes, such as heat or fluorescence, without being damaged itself. A functional test for such an ideal additive would be the suppression of molecular processes, such as the formation of vinylene unsaturation in polyethylene. It appears that more basic information regarding energy transfer in these systems is required before true protection by additives can be achieved.

It should be emphasized that the reported work on additive effects has been done on amorphous polymers (elastomers) and on semicrystalline polyethylene. For polymers of high degrees of crystallinity, it may be more difficult to obtain a homogeneous solution of the additive throughout the crystalline and amorphous regions of the material. In such cases the protective action of the additive may not be uniform throughout the polymer.

When highly crystalline or glasslike polymers are exposed to ionizing radiation, a new phenomenon occurs that is largely absent in soft, rubbery polymers or liquids. This phenomenon is the trapping of polymer radicals due to their immobility in the crystalline or glassy matrix.<sup>19, 20</sup> Reaction of these trapped radicals with oxygen can lead to significant postirradiation changes in the physical properties of the polymer. Since textile polymers usually possess

high degrees of crystallinity, it is appropriate to discuss this effect in more detail.

Lawton *et al.*<sup>19</sup> have studied the irradiation, by high-energy electrons, of a high-density, highly crystalline polyethylene (Phillips' Marlex-50). This material is about 90 per cent crystalline, compared to only about 40 per cent for ordinary, low-density polyethylene. The irradiation of this highly crystalline polyethylene at room temperature still produces C-H scission and vinylenic double bonds (reactions 1a and 2) but, rather than crosslinking (reaction 1b), the polymer radicals remain trapped. If the irradiated polymer is annealed

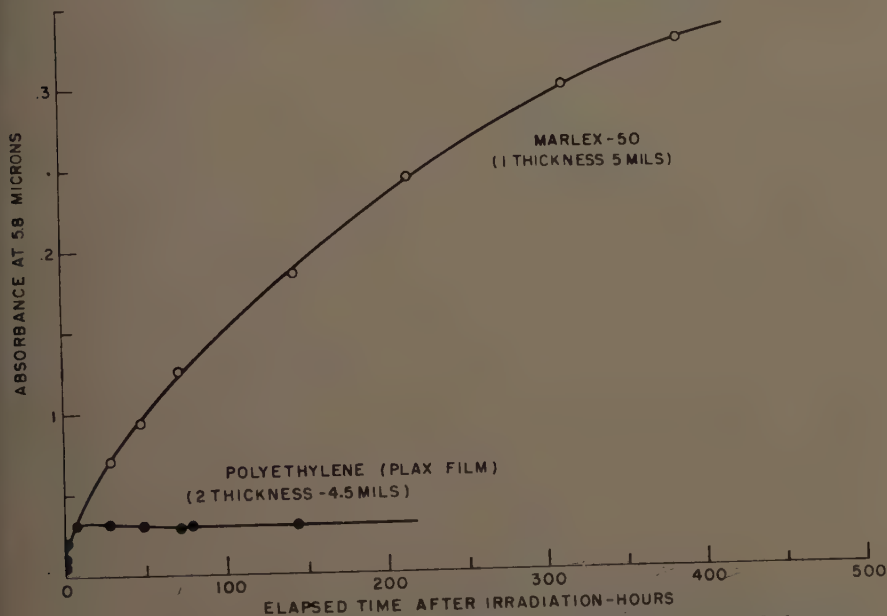


FIGURE 1. Delayed carbonyl formation in Marlex-50 and low-density polyethylene versus elapsed time after irradiation with 800 Kvp electrons. Irradiated to  $40 \times 10^6$  r in nitrogen. Samples stored in air.

at the crystal melting point ( $\sim 130^\circ$  C.), or if the polymer is irradiated while in the molten state, crosslinking occurs immediately, and there is no trapping of radicals.

Electron paramagnetic resonance measurements on Marlex-50, irradiated at room temperature and stored in the absence of oxygen, show an extremely slow decay of trapped radical concentration over a period of weeks following the irradiation. On the other hand, if the irradiated material is exposed to air or oxygen, a much more rapid decay of radicals occurs, with the production of carbonyl groups that appear at  $5.8 \mu$  in the infrared spectrum. FIGURE 1 shows the delayed formation of carbonyl groups following irradiation in ordinary polyethylene and in crystalline Marlex-50, both irradiated at a dose of  $40 \times 10^6$  r. In the less crystalline, ordinary polyethylene the carbonyl absorbance soon reaches a maximum value of only 0.03, while in Marlex-50 the

concentration of carbonyl is 10 times this value and still increasing 300 hours after irradiation.

The effect of postirradiation storage in air on the amount of crosslinking is shown in FIGURE 2. The upper curve represents the gel yield, which is a measure of the degree of crosslinking, as a function of dose for the irradiation of crystalline Marlex-50 in the molten state at 150° C. Under these conditions, immediate crosslinking occurs with no trapping of the polymer radicals. The lower curve shows the gel yields for samples irradiated in the crystalline state at room temperature and allowed to stand in air for 7 days before the crosslinking measurements were made. In this case the much lower gel yields

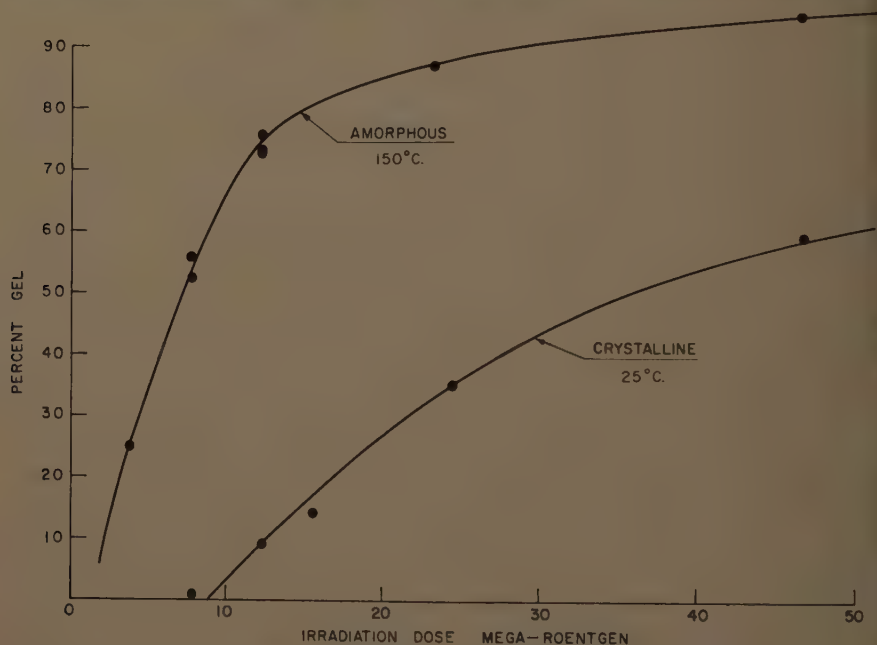


FIGURE 2. Gel yields versus irradiation dose for Marlex-50. *Upper curve:* samples irradiated in molten, amorphous state. *Lower curve:* samples irradiated in crystalline state and stored in air for 7 days prior to extraction in boiling toluene.

indicate that the major portion of the potential crosslinks have been lost by reaction with oxygen during the seven-day period following irradiation.

The change in the physical properties of the Marlex-50 due to this postirradiation oxidation was also examined by Lawton and his co-workers. In FIGURE 3 the solid curve A is the typical stress-strain behavior for unirradiated Marlex-50 at a low elongation rate of 0.5 in./min. The high modulus, up to the yield point, may be associated with the high degree of crystallinity, while the elongation beyond the yield point is determined largely by the molecular weight. Samples were irradiated with high-energy electrons at a dose of  $15 \times 10^6$  r at room temperature, and tensile measurements were made following storage in air for the periods indicated on the curve. With increasing storage time the elongation at the breaking point decreases, following the original curve until, at

128 days after irradiation, the sample is too brittle to measure. This behavior, together with independent chemical evidence, indicates that a degradation of the polymer chains can occur by reaction of the trapped polymer radicals with oxygen long after the irradiation. These results also emphasize the fact that, when trapped polymer radicals are formed by irradiation, the evaluation of radiation damage by a physical test alone can lead to an erroneous conclusion. Thus a tensile measurement, such as the one described here, made within one day after exposure to radiation, would show essentially no radiation damage. After standing in air for longer periods of time, however, the same material

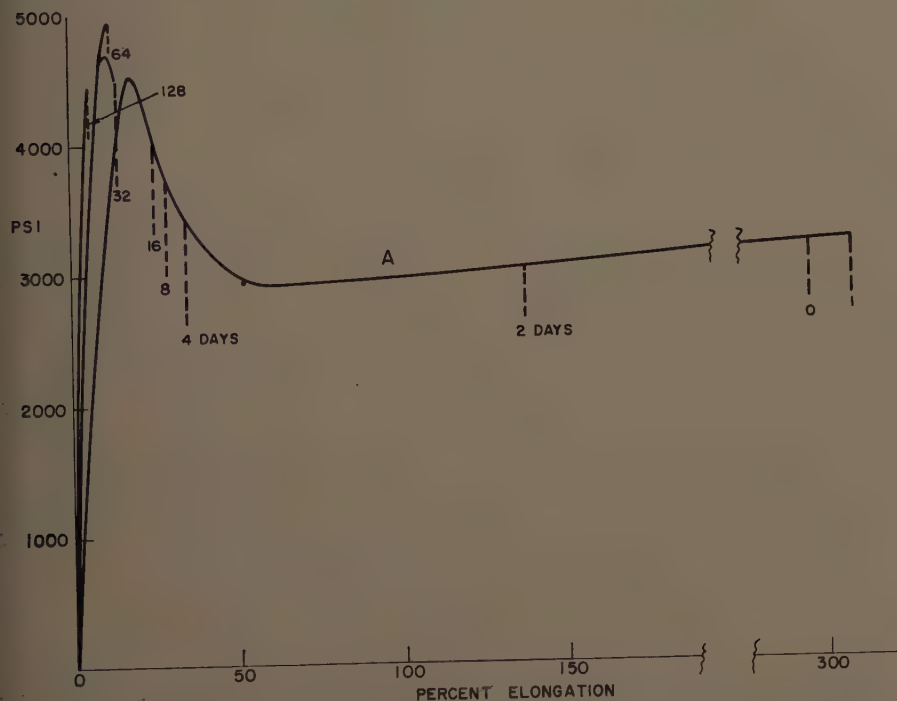


FIGURE 3. Stress-strain diagrams for Marlex-50 irradiated at 25° C. in nitrogen with 800 Kvp electrons. Samples stored in air for different periods of time before testing. Tensile tests at 25° C. at a crosshead speed of 0.5 in./min.

would show a severe loss of physical properties. In glasslike or highly crystalline polymers, therefore, it is important to ensure that no trapped radicals are present before any valid conclusion can be made regarding the radiation stability of the polymer based on measurements of physical properties.

In keeping with the major subject of this monograph, it is appropriate to examine briefly the possible effects of simultaneous irradiation and high temperature on organic polymers. Essentially all of the reported work on polymer irradiation has been done at room temperature, with occasional experiments up to 150° C. Over this limited temperature range, the increase in the yields of radiation-induced scissions or crosslinks is only about twofold.<sup>19, 21</sup> On the other hand, considerable information already exists on the mechanisms of

thermal degradation in the 250 to 400° C. temperature range, particularly for vinyl polymers. For these polymers, it is well established that the thermal degradations are free-radical chain reactions involving the four basic steps: initiation, propagation, transfer, and termination.<sup>22, 23</sup> Accordingly, it is reasonable to expect that the result of irradiation at high temperatures would be a free-radical chain degradation in which the thermal initiation step is augmented, or even supplanted, by radiation initiation. In such high-temperature irradiations involving a chain mechanism, the radiation intensity or dose rate should have a more pronounced effect than is observed for the non-chain crosslinking or scission effects that occur at ordinary temperatures. In this connection, there may be an interesting parallel with a reported study of the high-temperature (300 to 500° C.) radiation chemistry of hydrocarbons in the gas phase and comparisons with the purely thermal cracking of these materials.<sup>24</sup> In this work it was shown that the results could be satisfactorily explained by a radiation-initiated chain mechanism.

### Summary

The changes in physical properties of polymers under ionizing radiation are the result of crosslinking or scission of the polymer molecules; the process that predominates is, in turn, determined largely by the chemical structure. Polymers containing aromatic groups are usually the most radiation-resistant. In certain polymers free-radical inhibitors may retard the crosslinking process, but thus far we know of no true protective agent that at a low concentration will suppress all of the possible radiation chemical changes. In crystalline or glasslike polymers trapping of radicals may occur, and these can lead to post-irradiation effects that must be considered in assessing radiation resistance. For polymers that undergo thermal degradation by a free radical mechanism, exposure to ionizing radiation at high temperatures should result in an accelerated thermal degradation initiated by the radiation.

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# THE THERMAL STABILIZATION OF NYLON FIBERS\*

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## *Introduction*

The problem of the thermal deterioration of conventional organic fibers has at least three aspects that are so different that they are best treated separately. These are the three mechanisms involved in the thermal disintegration of organic solids by melting, oxidation, and pyrolysis. For further study, each of these aspects may be divided into more subproblems such as the part played by catalysis and auto-catalysis during oxidation, by the flammability due to the volatilization of the decomposition products during pyrolysis, and by the reaction of double bonds from dehydrogenation with free radicals from bond scissions, a reaction that will lead to crosslinking and charring and thereby to infusibility. It is the latter chain of processes that has been the main object of this investigation and that will be reported on in some detail below. A brief survey of the status of some of the other aspects will be given in order to present our work against this general background.

## *Brief Survey of Degradative Mechanisms*

Pyrolysis of organic fibers is frequently preceded and complicated by reactions of lower activation energy such as hydrolysis and oxidation, but in its pure form consists of processes of spontaneous bond scission due to supply of sufficient heat to provide the energy of activation for dissociation reactions. These activation energies are fairly widely spaced and thus allow a classification of bonds according to their strength. This is complicated by the fact that the initially first-order bond scissions will soon be accompanied by second-order interactions between reaction products and by intramolecular rearrangements.

In the case of macromolecules, with which we are here concerned, there exist several distinctive features. The early pyrolysis of vinyl polymers, for example, is characterized by the enhanced probability of random scission of one of the hundreds of backbone links and, second, by the fact that such splits will produce two free radicals that in many cases provide a ready mechanism of depolymerization by a zipperlike monomer-by-monomer split-off in an exact reversion of the polymerization mechanisms. These two mechanisms are fairly readily identified, the first by its strong effect on the average molecular weight, the other by the appearance of monomer as overriding decomposition product. TABLE 1 summarizes a variety of older data from the literature illustrating the two types of polymer decomposition, and FIGURE 1 shows schematically some of the reactions mentioned.

It should be noted that, accordingly, polymers liable to monomer by monomer degradation may become greatly stabilized by copolymerization with monomers not likely to split out readily from the chain ends. As for the nonzipping

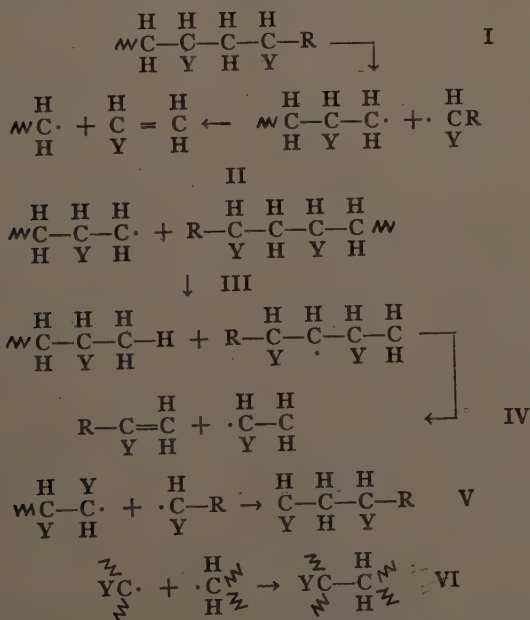
\* The work described in this paper was supported by the Clothing and Textile Division, United States Naval Supply Research and Development Facility Brooklyn, N. Y., under Research Contract No. N140(132)57745 B.

group, it is obviously important to avoid weak links in the chain. Weak links are those in which the activation energy of the transition state prior to scission is low. We do not know, in most cases, the nature and energy of the transi-

TABLE 1  
MONOMER YIELDS—VINYL POLYMER PYROLYSIS\*

Polymer	Percentage yield
Methyl methacrylate.....	90
$\alpha$ -Methylstyrene.....	90
Tetrafluoro ethylene.....	90
Styrene.....	50 to 90
Isoprene.....	50
Isobutylene.....	20 to 50
Methyl butadiene.....	25
Methyl acrylate.....	2
Ethylene.....	1

\* In absence of oxygen. Pyrolysis temperature 300 to 400° C. Solid residues show inverse trend.



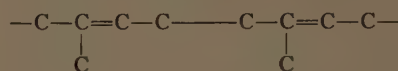
I. Homolytic scission. II. Depolymerization. III. Transfer.  
IV. Free radical cleavage. V, VI. Free radical recombinations.

FIGURE 1. Schematic polymer pyrolysis.

tion state, but the following example of relative readiness of bonds to break, shown in the case of natural rubber, FIGURE 2, seems to be frequently valid. Also illustrative is FIGURE 3, which contains selected groups in ascending order of readiness to decompose by radiation. These orders indicate that the relative ease of bond scission is largely influenced by the stability of the resulting

free radical, and should be compared with that of an approximate scale of radical reactivities shown in TABLE 2. The more stable a radical, the more readily will the scission occur that will produce it.

A related aspect concerns the liability of H-atoms or of side groups of the polymer chain to be attacked by free radicals and to develop branches, or to crosslink, or to lead to a weakening of the chain by oxidation. The column on the left-hand side of TABLE 2 arranges various groups according to their



H a b c d a b c

Relative Rate of Pyrolytic Break:

$a \approx 0$ ;  $b = 0.6$ ;  $c = 100$ ;  $d = 0.7$

FIGURE 2. Poly-cis-1,4-isoprene.<sup>7</sup>

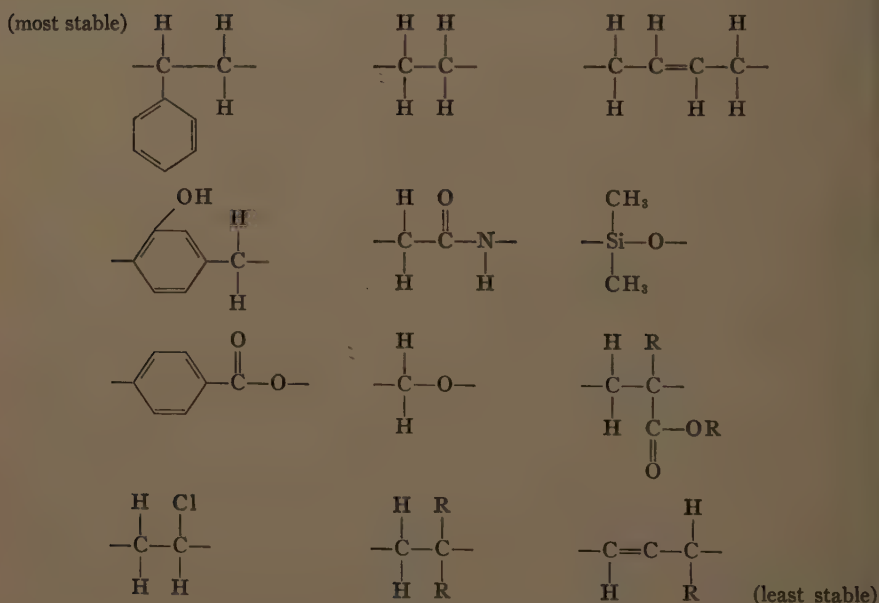


FIGURE 3. Relative cleavage stability.<sup>8</sup>

liability of becoming attacked and paving the way either to degradation, cross-linking or grafting, while the right-hand side shows the approximate reactivity (instability) of free radicals and thus the ability to attack the groups on the left.

Madorsky *et al.*<sup>1a, b, c</sup> recently carried out extensive work on the over-all stability of polymers, based on measurements of weight loss as a function of temperature and time. According to his results, the polymers may be divided into 3 groups: (1) those volatilizing readily at relatively low temperature; (2) those volatilizing slowly at much higher temperature; and (3) those volatilizing

to about 50 per cent, but then persisting in a charred state to rather high temperatures. Group (1) contains styrene, polyisobutylene and methacrylates; group (2) includes polyethylene, polyolefines, and perfluorinated olefines; while group (3) contains acrylonitrile (AN), vinylidenes, and crosslinked vinyl polymers. The behavior of AN and vinylidene polymers deserves attention. Their

TABLE 2  
APPROXIMATE ORDER

Ease of transfer	Free radical reactivity
$C=C-CHBr$ (greatest)	$H\cdot$ (greatest)
$C=C-CH_2OH$	$R_2CHCl$
$R_3CX$	$-CH_2-CH_2\cdot$
$RSH, R_2NH$	$CH_3\cdot$
$C=C-CH_2-R_2$	$RCOO\cdot$
$C=C-CHCl-$	$C_6H_5COO\cdot$
$-CH_2-O-CH_2-$	$RCH_2S\cdot$
$C_6H_5CO-$	$C_6H_5\cdot$
$-CH_2-CO-CH_2-$	$R_3C\cdot$
$-CH_2-CH(COOR)-$	$-CO-CH_2\cdot$
$C_6H_5-CH_2-R$	$-RO\cdot$
$ROOH$	$-CH_2-O-C\cdot H-R$
$-CH_2-CHR-$	$R_2C(CN)-$
$-CHO$	$C_6H_5CH_2\cdot$
$R_2CHOH$	$ROO\cdot$
$RCH_2COOH$	$CH_2=C-CHR$
$C_6H_6$	$R_2COH$
$-CH_2-CH_3$ (least)	$RCH_2-CHR$
	$RCOC_6H_4\cdot$ (least)

ability to char while maintaining some degree of structural coherence is due to their capacity to split out the corresponding hydro-halogen acid and to form double bonds. The resistance of crosslinked materials is due to the tie-in of broken chains into a network and the enhanced chance of radical recombination as compared to volatilization.

Resistance of polymers to pyrolysis thus will depend on whether breakdown occurs by unit or at random, and whether all the breakdown products are volatile or if some can reform to rebuild larger units, that is, on the balance

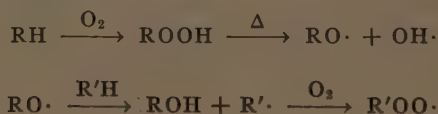


between volatilizing and crosslinking processes. Depicted schematically in FIGURE 1, the various courses shown will depend on the relative ease of primary bond breaks, hydrogen abstractions, monomer reformation, and radical recombination, depending on the nature of the substituent as pointed to in TABLE 2 and FIGURE 3.

Rounding out this section, we should mention an interesting investigation by Gruntfest<sup>2</sup>, who investigated the resistance of a wide variety of pure and filled plastics to very high temperatures. Although the exposure conditions are rather different, some of the important factors established by Gruntfest should also be of importance for fiber stability. Of these, a high melting point or infusibility, a high heat capacity, and a large gas volume per weight volatilized should be mentioned in addition to the factors discussed above.

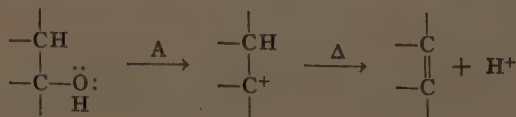
The stability of polymer to heating in air will be strongly dominated by its oxidizability. Alluding to this topic briefly, it can be understood readily that the same molecular groups that are liable to radical attack will be liable to oxidation also. These are primarily allylic and tertiary hydrogens, activated methylene groups, and groups such as those that neighbor amino-, keto-, and sulphydryl groups.

How the primary hydroperoxides are produced is not certain: whether by direct addition to carbon-bonded abstractable hydrogens or whether the hydrogens must be abstracted first by radicals that stem from thermal decomposition. The hydroperoxides then split into free radicals that add oxygen to form peroxy radicals that can decompose, or abstract, hydrogens themselves, shown schematically as:



In any event, a chain is set up that is carried by oxygen until radical recombination occurs.

Cellulose and its derivatives belong to the thermally labile compounds, and range near the bottom of every stability list. Native and regenerated celluloses therefore have been the object of innumerable attempts at flameproofing, afterglow reduction, or general thermal stabilization. TABLE 3 gives a brief survey of some of the more successful methods. The main activity of the flameproofing agent seems to be to act as Lewis acids and as such to enhance the stabilization of carbonium ions and subsequent dehydration of hydroxy compounds.



In a very thorough recent study, Pacsu and his co-workers<sup>3</sup> at the Textile Research Institute, Princeton, N. J., have succeeded in establishing the most important step responsible for the low thermal stability, especially flammability, of cellulose. It is the formation of Levoglucosan which, as a very reactive keto acid, enhances rapid oxidation to the point of inflammation. TABLE 3

shows their analysis of cotton pyrolysates. When the labile hydrogen of the primary alcohol group becomes substituted, much better thermal stability results. The greatest improvement comes from a partial mesytilation followed by replacement of the mesyloxy group by bromine. The remainder of the cellulose is then phosphorylated to suppress cotton afterglow. The correspond-

TABLE 3  
LIST OF TYPICAL FLAME-PROOFING AGENTS

Type compound
1. Ammonium compounds of boric and phosphoric acids <sup>9</sup>
2. Urea, Guanidine, cyanamide in combination with phosphoric acid <sup>9</sup>
3. Antimony, zinc and tin in combination with halogenated organic compounds <sup>9</sup>
4. Titanium compounds as orthoesters <sup>10</sup>
5. Alkanol amine sulfamates <sup>11</sup>
6. THPC method; copolymerization of tetrakis hydromethyl phosphorus chloride and methylol melamine <sup>12a, b</sup>
7. BAP method: emulsion of polymer of triallyl phosphate <sup>13</sup> and bromoform
8. Combination of THPC and BAP <sup>14</sup>
9. Bromine containing phosphonitriles <sup>15</sup>

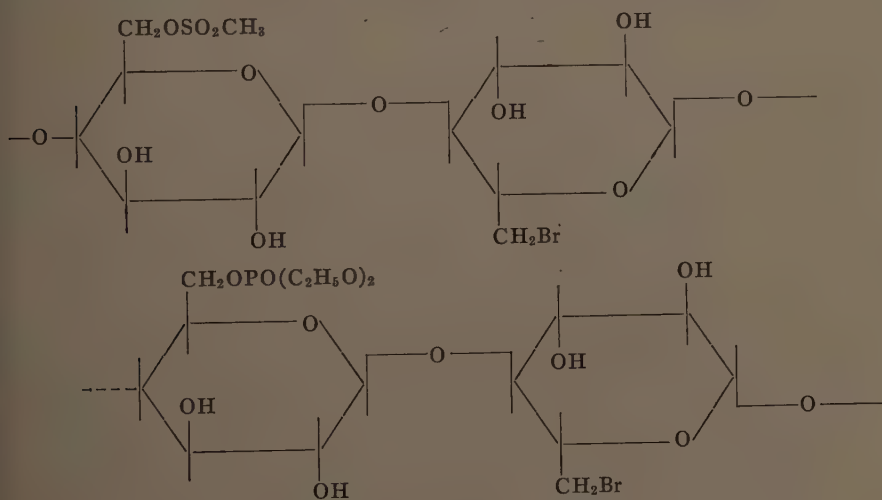


FIGURE 4. T R I—modified cellulose.

ing structures are shown in FIGURE 4. Incidentally, wet cotton exhibits excellent flame resistance.

The thermal degradation of polyesters has not been as widely investigated. However, it has been established that they are inferior to most other polymers. From the work of Marshall and Todd<sup>4</sup> on Dacron, it appears that decarboxylation after a random chain scission is the prevalent mechanism; it is accelerated by oxygen and by water that is quantitatively consumed by hydrolysis. Altogether, in all degradation processes, the importance of traces of oxygen or of impurities in catalyzing or changing the degradation mechanisms cannot be overemphasized.

Turning to polyamides, it is well known that most of them, including wool, silk, and the nylons, exhibit well-defined melting processes. However, the melting points are so close to, or above, the decomposition temperature that discolorations occur and charring reactions become important. Kline, his co-workers and Madorsky, during the pyrolysis of 6-6 nylon at 400 ° C., found water, carbon monoxide, hydrocarbons, and cyclo pentanone and 5 per cent of other gaseous products, including ammonia, amines, and carbon dioxide. It

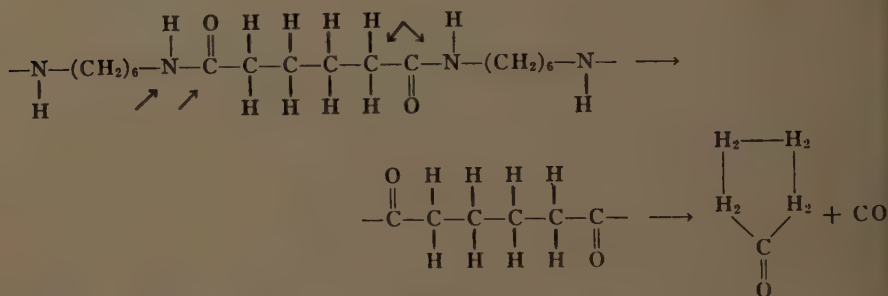


FIGURE 5. Degradation of 6-6 nylon.

TABLE 4  
ANALYSIS OF UNMODIFIED COTTON CELLULOSE PYROLYSATE

Product	Per cent yield
Levogluconan	12.5
Carbonyl compounds	ca. 15.0
(1) Formaldehyde	
(2) Glyoxal	
(3) Unidentified	
Acidic compounds	7.5
(1) Formic or acetic acid	
(2) Glycolic acid	
(3) Lactic acid	
(4) Dilactic acid	
(5) Unidentified	
Water	ca. 55.0
Unknowns	10.0
	100.0

must be added that different results applied to other polyamides, and that greater amounts of amides were reported by Hasselstrom<sup>5</sup> and by Goodman.<sup>6</sup>

To account for these observations, it is necessary to assume chain scission at the  $-\text{CH}_2-\text{CO}-$  bond as well as at the  $-\text{CO}-\text{NH}-$  bond, as shown on FIGURE 5. The formation of ammonia requires hydrogenation of some amines and formation of  $\alpha$ -olefines that may be held responsible for crosslinking. The formation of cyclohexanone is significant in a particular way. Forming from a chain element, this ring represents a very stable breakdown product, and as such enhances decomposition reactions. Quite generally, it has been found that whenever a chain molecule possesses units 5 to 7 backbone atoms long, its thermal stability is impaired by the ease with which rings break out

anywhere from the chain. This need not be a free radical reaction but can, for example, be the reverse of a transamidation as in the case of  $\epsilon$ -caprolactam.

### *The Melt Proofing of Nylon*

The decomposition of nylon, however, is of secondary importance for its serviceability as a textile as compared with the process of melting. Consequently, melt prevention received our primary attention. Our approach was directed at either crosslinking nylon superficially by reaction with trifunctional compounds, in view of the early splitting out of carbon monoxide, mainly tri-

TABLE 5

Compound	Thermal resistance	P per-cent-age	Polymer
I. $C_6H_5PO(OCH_2-CH-CH_2)_2$	good	13.0	hard glassy
II. $CH_3PO(OCH_2-CH=CH_2)_2$	good	17.6	moderately hard flexible
III. $ClCH_2PO(OCH_2-CH=CH_2)_2$	good	14.7	moderately hard flexible
IV. $nC_4H_9PO(OCH_2-CH=CH_2)_2$	fair	14.4	—
V. $OP(OCH_2-CH=CH_2)_3$	poor	14.2	—
VI. $HPO(OCH_2-CH=CH_2)_2$	very poor	19.2	glassy

TABLE 6

Compound	Appearance	Solubility in		
		Water	EtOH	Hydro-carbons
1. Tetra isopropyl titanate (TPT)	colorless liquid	decomp.	sol.	sol.
2. Tetra n-butyl titanate (TBT)	lt. yellow liquid	decomp.	sol.	sol.
3. Tetra Q-ethyl hexyl titanate (TOT)	lt. yellow	decomp.	sol.	sol.
4. Octylene glycol titanate (OGT21)	solid	insol.	sol.	v. sol.
5. Octylene glycol titanate (OGT21 washed)	solid	insol.	sol.	v. sol.
6. Triethanol amine titanate (TAT21)	liquid	sol.*	sol.	insol.
7. Titanium lactate (TiLac)	solid	v. sol.	sl. sol.	insol.

\* Hydrolyzes on standing 24 hours.

basic acids, or at coating the individual filaments by nonfusible, either cross-linked or self-crosslinking materials. The prognosis for the latter approach was not promising because it had been repeatedly reported that all attempts at flameproofing of nylon by coatings had led to a much accelerated thermal decomposition. However, our early experiments led to an opposite result; we had very little success with crosslinking and the application of such time-honored stabilizers as phosphorus, boron, titanium, or chlorine-containing compounds. TABLES 5 and 6 show some of the phosphorus compounds and titanium esters that were tried. On the other hand, promising results were obtained with infusible polymer coatings, especially polyacrylamide and polyacrylonitrile; the latter is preferable because of its insolubility in water.

In the application of thin polymer coatings to nylon filaments or fibers, great difficulties were encountered with respect to the method of fixation. A large number of attempts to graft from a bath solution failed, even when the solvents such as concentrated sulfuric acid or dimethyl formamide were capable of swelling nylon appreciably. Apparently, only minor amounts of catalyst or polymer penetrate the fibers by diffusion. If the fibers are first swelled by concentrated solutions of catalyst and then immersed in monomer or in monomer solution, the catalyst apparently is eluted too quickly to allow appreciable initiation to occur in deeper fiber layers. Similarly, an extensive study of chain transfer in polymerizing systems to immersed nylon revealed that the transfer constants of the growing polymer chains to nylon were too small to allow significant grafting to take place. We shall return to this important point below.

Failing to obtain sufficiently permanent catalyst imbedding or large-scale transfer, we tried various surface modifications, such as reacting the amide hydrogen with methacryl or succinyl chloride, followed by reaction with cumene hydroperoxide, so as to append initiating succinyl cumene peroxide. The recently published method of nitrosylation, leading to nitroso acetanilide acetate, and providing initiating azo compound was also applied. In every case, we met only with moderate success, notwithstanding the fact that the desired surface modification was achieved, because the ensuing grafting led to polymer coatings that were either too thin or too imperfect.

Final progress was eventually made with a variation of Speakman's method of impregnating wool. The fibers, or fabrics, were soaked in aqueous persulfate solution, superficially dried, and exposed to monomer vapor, in particular to acrylonitrile. Although not entirely uniform, the coatings were more regular than by other methods; their thickness was easily regulated by way of exposure times; and the fibers retained their original texture better than by any other method.

Samples of fabric were submerged in aqueous solutions of  $K_2S_2O_8$  for 20 min. This allowed the  $K_2S_2O_8$  to adsorb on the surface and to diffuse into the amorphous areas of the fibers. The reaction apparatus is shown in FIGURE 6. Inhibited acrylonitrile is refluxed with cocks 1 and 2 closed. A heating strip around tube A heats the tube to the boiling point of acrylonitrile. When the liquid is refluxing and the temperature in tube A has reached the boiling point of acrylonitrile, the sample supported on a hook in a rubber stopper is inserted into tube A. At this point cocks 1 and 2 are opened, and the time is checked. This will allow the acrylonitrile vapors to surround the sample immediately and then reflux into flask B. After the required period of time, the cocks are closed again and the sample is recovered. The sample is washed in water several times and dried. Variables studied in this experiment are: (1) the duration of treatment (1, 2, 5, 10, and 30 min.); (2) the concentration of the initiator in the pretreatment solution (0.1, 0.2, 0.5, 1.0, and 2.0 per cent); and (3) the initiators used.

The apparatus shown in FIGURE 7 was developed to enable rapid testing of the behavior on heating of threads taken from treated fabrics. A nitrogen atmosphere is employed instead of air in order to eliminate the effect of oxygen on the melting point. The temperature within the tube was adjusted by



means of a powerstat. The method employed in observing the behavior on heating was as follows:

A thread from the treated fabric extending about one and a half inches from the end of the guide tube is hung in the apparatus and its length and appearance at  $240^{\circ}\text{C}$ . are noted. Untreated samples of nylon begin to melt at the lower tip whenever the melting point of about  $260^{\circ}\text{C}$ . is reached. As more of the thread melts, there is extensive shrinkage in length and, when the weight of

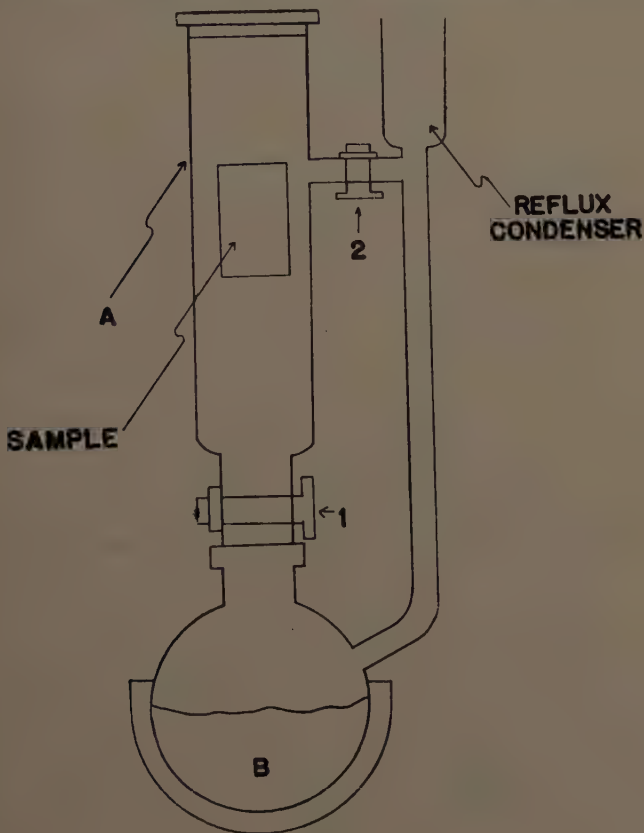


FIGURE 6.

the melted portion can no longer be supported by the remainder of the thread the melted portion or bead breaks away.

Fibers that have been effectively treated show a different behavior on being subjected to the same temperature range and rate of heating. We found samples which, although the thread showed signs of melting, exhibited no tendency to flow or drip from the rest of the thread. Another group of samples show no evidence of melting, but the individual filaments of the threads remain separate and distinct until charring occurs. There is, of course, a gradation of behavior between these two extremes. We believe that this distinction is a valuable one and that our test affords a decision as regards the qualitative effectiveness of a particular treatment.

On comparing the effect of treatment on fabric as received and that on boiled-off fabric, a large difference in the nature of the deposit was observed. The fabric as received yielded a flaky polyacrylonitrile deposit, the extent of flakiness dependent on the extent of the treatment. The boiled-off fabric gave a much more uniform, visibly undetectable deposit, the amount of which depended on the treatment. This may be explained by assuming that on boiled-off fabric the free radical attack occurs on the nylon itself while, in the

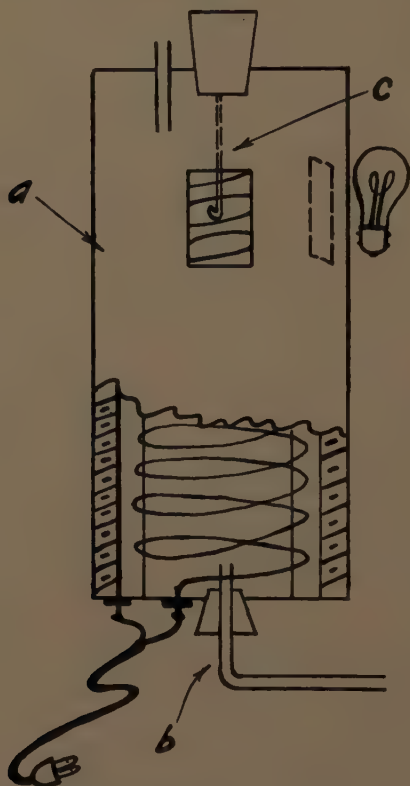


FIGURE 7. (a) Outer tube lagged with asbestos with window at thermometer bulb level; (b) nitrogen inlet; and (c) thermometer to 360° C.

case of sized fabric, the attack occurs on the coating that shielded the underlying nylon. As a consequence, all work was carried out on boiled-off fabrics, and all results refer to data obtained in that way.

In summary: (1) aqueous solutions of potassium persulfate or a combination of this with sodium bisulfite, as well as benzoyl peroxide in ethyl alcohol, have been used as catalysts for the polymerization of acrylonitrile in the vapor phase. In all cases tried, the  $S_2O_8^{2-}$ — $HSO_3^-$  redox system deposited the greatest amounts of polymer.

(2) As the time of exposure was lengthened, the amounts of deposited polymer increased. Some samples after treatment were washed repeatedly

in dimethyl formamide to remove excess polymer, and then dried to constant weight. Up to 75 per cent of the coating was thereby found to be removable.

(3) As the concentration of catalyst was increased, the amount, both extractable and nonextractable, of polymer deposited on the fabric increased.

(4) Depending on the amount of the deposited polymer, the melt resistance of the treated fibers ranged from unchanged, with the mildest treatment, to softening without melting for medium coatings, whereby the individual fibers fused in a single filament without further flow. The heaviest treatment, the flakiest coating, resulted in charring and shrinking of the fibers, also without melting.

### Discussion and Conclusions

To summarize briefly the meaning of the results and the further steps indicated, no dipping treatment of nylon fibers is by itself likely to lead to satisfactory results. If the catalyst is supplied to the fiber surface by a soaking solution, monomer vapor exposure must follow; if the dipping provided a polymeric coating, a similar exposure by a crosslinking agent must be applied. The reason for the failure of one-step treatments must be attributed to the fact, hitherto unexplored, that, notwithstanding the presence of three somewhat activated hydrogen atoms on the  $\text{—CH—N—C—CH—}$  grouping, chain



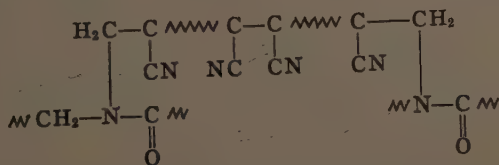
transfer by free radical attack on these hydrogens is slow. Thus, true grafting on the nylon chains during a polymerization process, either as a homogeneous or heterogeneous reaction, is rather limited and one must predeposit catalyst into the fiber surfaces in order to grow a coating sheath around them.

Considering the inhibition of melting by the *in situ* polymerization of acrylonitrile or acrylamide on the fiber surfaces, we can envisage several modes of action:

(1) Since these polymers are themselves infusible (that is, they decompose below melting), one might simply think of a supporting sheath. The argument against this is that dip coating with polyacrylonitrile from solution does not delay nylon melting.

(2) Inasmuch as some polymer may have grafted on amide groups, this amounts to a sparsely anchored polymer sheath, and the same failure should result again; moreover, nylon-acrylonitrile grafts should be readily soluble in the nylon melt.

(3) Consequently, one must think of a crosslinking mechanism of considerable effectiveness, all the more so since most probably only a thin surface layer is involved in the melting-delay mechanism. Crosslinking by graft



bridges would be insufficient. The crosslinking must be much denser. A regular copolymerization is not possible, so that one is led to the assumption

that in our coating process either the acrylonitrile coating penetrates to some depth or that a reaction between nylon and acrylonitrile occurs at the melt temperature.

We know that heated polyacrylonitrile tends to form rings along its chains and that this process is enhanced by amines and bases. The amine groups of decomposing nylon can act in the latter function. This may be depicted as shown in FIGURE 8. We assume then that the major crosslinking processes occur at the melting stage between amide groups, or amine end-groups of the nylon and decomposition products of the partly degraded acrylonitrile chains.

The same type of mechanism may be postulated also for the melt protection by any other polymer coating, which in itself does not melt or volatilize. Examples may be polyvinyl pyrrolidone, poly  $\alpha$ -amino acids, and polymers containing nonvolatile acids, such as phosphoric acid residues.

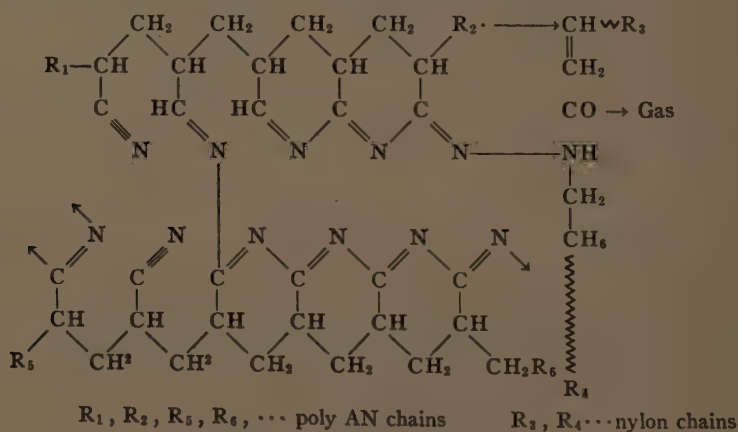


FIGURE 8. Potential crosslinking sites.

In view of this deduction, it is somewhat surprising that we met with little success when crosslinking acid agents were applied to the surface. This may be due to poor reaction, but more probably is due to the fact that the crosslinks formed by polycarbonic acids are themselves not sufficiently heat-resistant to high temperatures, and break down by decarboxylation.

The latter suggestion leads to the topic of inhibition of thermal degradation as distinct from melt prevention. It is well known that all degradation reactions proceed more readily in the melted state, partly because of its higher entropy and partly because of the enhancement of diffusion and convection. Therefore, thermal stability represents a smaller problem, if melting can be prevented. Metal compounds, stable acids, and high-temperature radical sources similar to allyl and halogen compounds were found moderately successful, very likely because their efficiency to block end groups is compounded by an ability to aid cross linking.

In conclusion, we believe that our results show that our approach has led to encouraging findings. Without quoting individual results, we established the principle of effective prevention of fiber melting by depositing surface



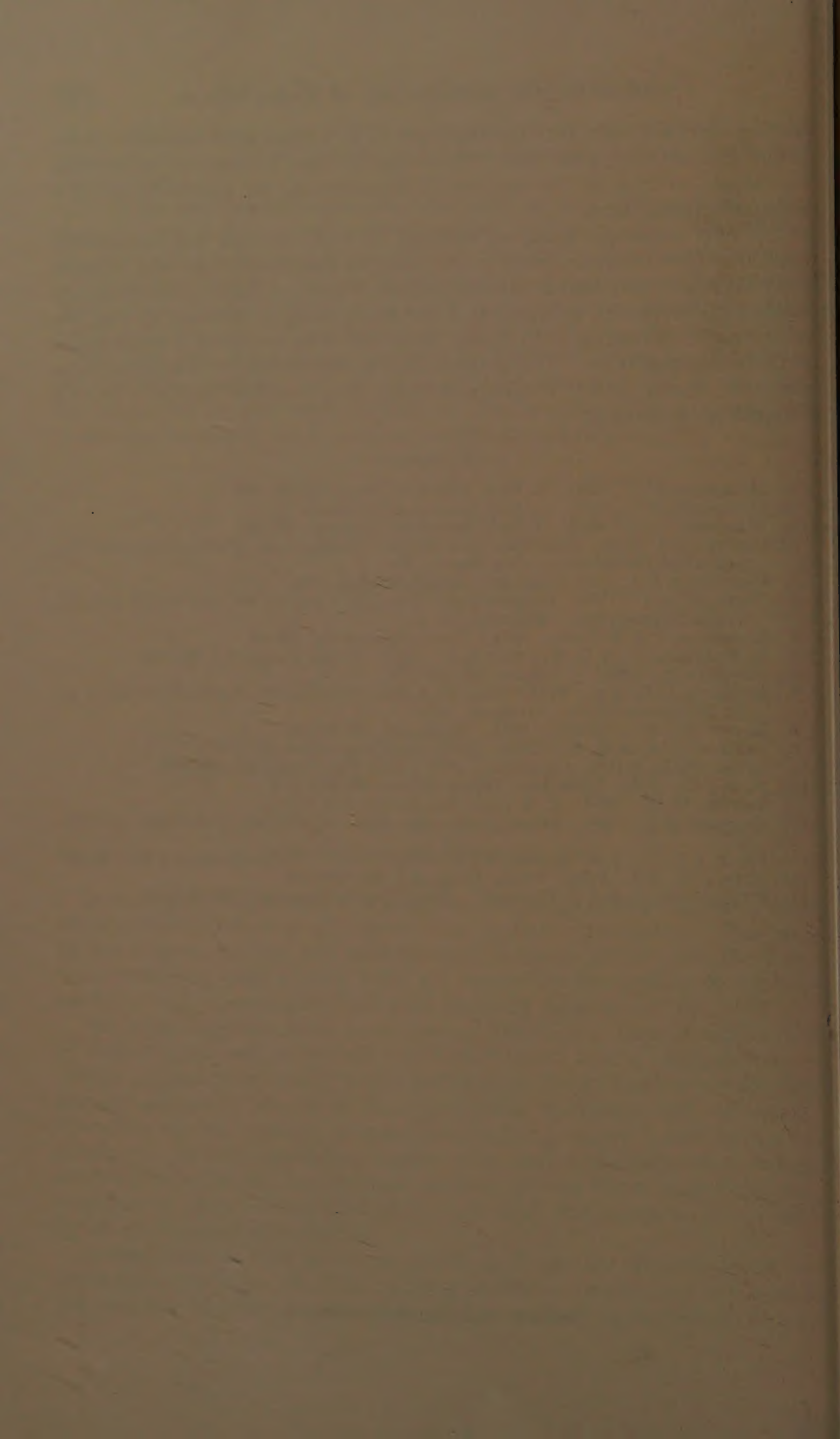
coatings that will react with the fiber melt so as to lead to an infusible sheath around the softening fiber core. These coatings may or may not be infusible themselves, as long as the reaction leads quickly to the establishment of a resistant infusible bark.

The next important group of findings, in itself not new but successfully applied to fiber behavior, refers to the principle that crosslinking of a polymer (here, of nylon) may lead to infusibility even if it be so slight as not to impair mechanical properties, provided that the crosslinking is sufficient to stop the fiber from early melting until denser self-crosslinking occurs as a consequence of thermal degradation. This is known as heat embrittlement in rubbers, polyethylene, styrene, and in a variety of fibers, and is utilized here as a process competitive to melting.

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